



# TECHNICAL NOTE

423

## Electrochemical Analysis Section:

**SUMMARY OF ACTIVITIES  
JULY 1966 TO JUNE 1967**



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**U.S. DEPARTMENT OF COMMERCE  
National Bureau of Standards**

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# TECHNICAL NOTE 423

ISSUED OCTOBER 1967

Electrochemical  
Analysis Section:

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Edited by Roger G. Bates

Electrochemical Analysis Section  
Analytical Chemistry Division  
Institute for Materials Research

NBS Technical Notes are designed to supplement the Bureau's regular publications program. They provide a means for making available scientific data that are of transient or limited interest. Technical Notes may be listed or referred to in the open literature.

## FOREWORD

The Analytical Chemistry Division was established as a separate division at the National Bureau of Standards on September 1, 1963, and became part of the Institute for Materials Research in the February 1, 1964, reorganization. It consists at present of nine sections and about 100 technical personnel encompassing some 45 different analytical competences from activation analysis and atomic absorption to vacuum fusion and x-ray spectroscopy. These competences, and in turn the sections which they comprise, are charged with research at the forefront of analysis as well as awareness of the practical sample, be it standard reference material or service analysis. In addition it is their responsibility to inform others of their efforts.

Formal publication in scientific periodicals is a highly important output of our laboratories. In addition, however, it has been our experience that informal, annual summaries of progress describing efforts of the past year can be very valuable in disseminating information about our programs. A word is perhaps in order about the philosophy of these yearly progress reports. In any research program a large amount of information is obtained and techniques developed which never find their way into the literature. This includes the "negative results" which are so disappointing and unspectacular but which can often save others considerable work. Of importance also are the numerous small items which are often explored in a few days and which are not important enough to warrant publication--yet can be of great interest and use to specialists in a given area. Finally there are the experimental techniques and procedures, the designs and modifications of equipment, etc., which often require months to perfect and yet all too often must be covered in only a line or two of a journal article.

Thus our progress reports endeavor to present this information which we have struggled to obtain and which we feel might be of some help to others. Certain areas which it appears will not be treated fully in regular publications are considered in some detail here. Other results which are being written up for publication in the journal literature are covered in a much more abbreviated form.

At the National Bureau of Standards publications such as these fit logically into the category of a Technical Note. In 1967 we plan to issue these summaries for all of our sections. The following is the third annual report on progress of the Electrochemical Analysis Section.

W. Wayne Meinke, Chief  
Analytical Chemistry Division

## PREFACE

This is the third annual progress report of the Electrochemical Analysis Section of the Analytical Chemistry Division. The report covers the fiscal year 1967, which began on July 1, 1966, and ended on June 30, 1967.

The Section concerns itself particularly with ionic processes occurring in solution, with areas of analytical measurement where ionic equilibria play a part, and with the explanation of solution behavior in terms of the interactions of ionic solutes with solvent molecules. We do not attempt to cover the entire field of electrochemistry or even of electroanalytical chemistry. The special interests of members of the Section lie for the most part in solution electrochemistry, electrochemical thermodynamics, and ionic transport phenomena. In the context of modern analytical chemistry, their competences bear most directly on potentiometry, electrometric titrations, and conductometric analysis. In line with a uniform policy of the Division, the Section's programs have both research and sample aspects. During the fiscal year just ending, about 70 percent of the total effort was devoted to research while 30 percent was devoted to Standard Reference Materials.

The permanent staff of the Section was reduced by four during the year, and understaffing inevitably left its imprint on the progress of our research programs. At the conclusion of their appointments as Commerce Science and Technology fellows, Dr. Robert Gary and Dr. Richard K. Wolford accepted positions in scientific administration outside the Division. Later in the year Vincent E. Bower and Cyrus G. Malmberg left the Section by transfer to other NBS Divisions. However, Dr. Bert R. Staples joined the

Section in May. In September Dr. Donald Rosenthal came to us in the capacity of Visiting Expert and remained until February. During the same period, James T. Clark, Jr., a graduate student of Dr. Rosenthal, was a Guest Worker in the Section. Philip K. Hall of the University of Wisconsin at Marshfield joined us for the summer of 1966.

The purpose of this report is to summarize the total activity of the Electrochemical Analysis Section during the reporting period. Unlike the formal journal publications that emanate from the Section, this report offers an opportunity to present the program as an integrated whole, to set forth the objectives of this specialized group, and to underscore the relationships between the Section's activities and the missions of the Division and Institute.

In order to specify adequately the procedures, it has been necessary occasionally to identify commercial materials and equipment in this report. In no case does such identification imply recommendation or endorsement by the National Bureau of Standards, nor does it imply that the material or equipment identified is necessarily the best available for the purpose.

The assistance of Mrs. Rosemary Maddock, Mrs. Marguerite Raudenbush, and Robert J. Boreni in the preparation of this report is gratefully acknowledged.

Roger G. Bates, Chief  
Electrochemical Analysis Section

Washington, D.C.

June 30, 1967

TABLE OF CONTENTS

	PAGE
1. FACILITIES AND EQUIPMENT . . . . .	1
Space and Equipment . . . . .	1
Plans and Needs . . . . .	4
2. MEASUREMENT OF ACIDITY . . . . .	6
Concepts and Program . . . . .	6
pH Standards: Sodium Hydrogen Succinate . . . . .	8
pH* Standardization: Status of Acidity Standards for Alcohol-Water Media . . . . .	10
pD Standards . . . . .	13
Present Status . . . . .	13
Potassium Dihydrogen Citrate . . . . .	16
Measurement of Acidity in Biological Media . . . . .	18
Measurement of Acidity in Sea Water . . . . .	20
Behavior of Glass Electrodes in Deuterium Oxide . . . . .	22
Method . . . . .	23
Experimental . . . . .	25
Results . . . . .	25
3. SOLVENT EFFECTS ON IONIC PROCESSES . . . . .	29
Ion-Solvent Interactions . . . . .	29
Medium Effects for Chlorides in Methanol- Water Solvents . . . . .	31
Medium Effects for Individual Ionic Species . . . . .	35
Potentiometric Studies in N-Methylpropionamide . . . . .	38
Acid-Base Behavior in Aprotic Organic Solvents . . . . .	39

	PAGE
4. EQUILIBRIUM DATA FOR IONIC SYSTEMS . . . . .	40
Dissociation of Piperazinium Ions in Water . . .	40
Dissociation Constants of Substituted Anilines and Phenols . . . . .	45
Isopiestic Vapor Pressure Measurements . . . . .	47
Spectrophotometric Studies in N-Methylpropionamide . . . . .	48
5. CONDUCTANCE AND TRANSPORT BEHAVIOR OF ELECTROLYTES . . . . .	49
Objectives and Approach . . . . .	49
Analysis of Errors of the Jones-Dike Conductance Bridge . . . . .	50
6. PREPARATION AND PROPERTIES OF SOLVENTS . . . . .	54
Ethanol (95 Volume Percent) . . . . .	54
N-Methylpropionamide . . . . .	56
7. NONAQUEOUS TITRATIONS: DETERMINATION OF HYDROGEN FLUORIDE . . . . .	62
8. FOREIGN-CURRENCY PROGRAMS . . . . .	66
9. IMPACT OF SECTION'S ACTIVITIES . . . . .	67
10. PERSONNEL . . . . .	68
11. COMMITTEE MEMBERSHIPS . . . . .	69
12. PUBLICATIONS AND MANUSCRIPTS, JULY 1966 TO JUNE 1967 . . . . .	70
13. TALKS, JULY 1966 TO JUNE 1967 . . . . .	73
14. LIST OF REFERENCES . . . . .	75

## LIST OF FIGURES

FIGURE NO.	PAGE
1. One of the emf laboratories . . . . .	1
2. Laboratory for conductance studies . . . . .	2
3. Equipment for precise emf measurements with glass electrodes . . . . .	2
4. Assembly of equipment for electrometric titrations . . . . .	9
5. Assembly of apparatus for studies of the behavior of glass electrodes in heavy water . . . . .	26
6. Emf cell used for the direct and indirect comparison of glass electrodes with the deuterium gas electrode in heavy water . .	27
7. Emf cell with liquid junction, containing a calomel electrode prepared with heavy water . . . . .	27
8. Direct comparison of two glass electrodes with deuterium gas electrode over a range of pD . . . . .	28
9. Differences between the medium effects for individual ionic species in methanol-water solvents . . . . .	34
10. Extrapolation curve for obtaining $pK_1$ from the values of $pK_1'$ . . . . .	42
11. Variation of $pK_1$ for piperazinium ion with temperature . . . . .	44
12. Relationship between the pK of substituted protonated anilines ( $pK_A$ ) and that of the corresponding substituted phenols ( $pK_P$ ) . . . . .	46
13. Switch panel used with conductance bridge to provide a resistor in series or parallel with the cell and to reverse the cell leads . . . . .	53
14. Cell used for measurements of relative dielectric constants in NMP and NMP-cyclohexane mixtures . . . . .	57

LIST OF FIGURES (con't)

FIGURE NO.	PAGE
15. Excess molar volume ( $V_{12-N_1V_1-N_2V_2}$ ) of NMP-water mixtures at 30 °C as a function of the mole fraction of water ( $N_2$ ) . . . . .	59
16. Dielectric constant deviations ( $D_{12-N_1D_1-N_2D_2}$ ) of NMP-water mixtures at 20, 30, and 40 °C as a function of the mole fraction of water ( $N_2$ ) . . . . .	60

LIST OF TABLES

TABLE NO.	PAGE
1. Stability of cells of the type Pt;H <sub>2</sub> , NaHSuc (0.02m), KCl (m), AgCl;Ag . . . . .	10
2. Standard values of pH*(S) in 50 wt percent methanol . . . . .	11
3. Standard reference values of p <sub>aD</sub> for an acetate buffer solution and a phosphate buffer solution in deuterium oxide from 5 to 50 °C . . . . .	14
4. Correction factors for operational pD measurements in heavy water solutions . .	26
5. Medium effects for chloride salts in methanol-water solvents at 25 °C . . . . .	33
6. Medium effects ( $\log m^{\gamma}_H$ ) for the transfer of hydrogen ion from water to methanol-water solvents . . . . .	37
7. Comparison of thermodynamic constants for the dissociation of piperazinium, morpholinium, piperidinium, and pyrrolidinium ions at 25 °C . . . . .	43
8. Dielectric constants of N-methylpropionamide-cyclohexane mixtures at 25 °C . . . . .	61
9. Analysis of variance for fluoride titrations . . . . .	64
10. Analysis of variance for standardization of base . . . . .	64

ELECTROCHEMICAL ANALYSIS SECTION: SUMMARY OF ACTIVITIES,  
JULY 1966 TO JUNE 1967

Edited by Roger G. Bates

ABSTRACT

This survey of the activities of the Electrochemical Analysis Section, Analytical Chemistry Division, covers the period July 1966 to June 1967. An attempt is made to summarize a year's progress on the technical projects of the Section in such a way as to stress the program and capabilities of the organizational unit as a whole. A description of facilities and equipment is presented, and the directions of the programs are indicated. Brief summaries of several lines of work now under way are given. The main areas include the measurement of acidity, with progress toward the establishment of standards for pH, pH\*, and pD being reported. Studies of the behavior of glass electrodes in deuterium oxide are described and solvent effects on ionic processes are discussed. Equilibrium data for certain ionic systems have been obtained, modifications of a precision conductance bridge are described, and a method for titrating hydrogen fluoride in dimethylformamide is outlined. The survey concludes with lists of the members of the Section staff, publications and manuscripts produced during the year, talks given by the staff, and committee assignments.

Key Words

Electrochemical analysis, Analysis, Acidity, Glass electrodes, pH measurements, Medium effects, Conductance measurements, Electrochemistry of solutions

## 1. FACILITIES AND EQUIPMENT

### A. Space and Equipment

As presently arranged, the Section's facilities and equipment provide five well-equipped laboratories for highly accurate emf measurements, a conductivity laboratory, an instrumentation room, a solvents preparation laboratory, a balance room, and space for spectrophotometric and isopiestic vapor pressure studies. One of the emf laboratories is shown in figure 1 and a corner of the conductance laboratory is seen in figure 2.



Figure 1. One of the emf laboratories.

Four new constant-temperature baths of stainless-steel construction were received during the year. One of them can be seen in figure 3. These thermostats are provided with 1/2-hp built-in compressors which, in spite of a rather

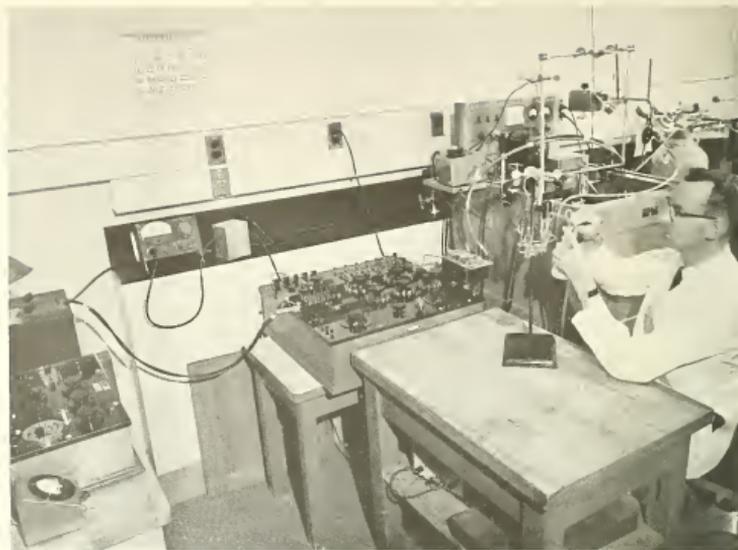


Figure 2. Laboratory for conductance studies.



Figure 3. Equipment for precise emf measurements with glass electrodes.

high noise level, appear to function satisfactorily when properly adjusted. Considerable delay was involved, however, before the manufacturer succeeded in putting the controls into a condition which warranted acceptance. Further modifications were then necessary in order to provide each bath with a brass framework to support the cells and a manifold to distribute the purified hydrogen gas. Improved temperature control was also provided by external commercial electronic controllers of the proportional type utilizing thermistor sensors. Although these have proved generally satisfactory, they are not entirely free from drifts which become evident when a constant setting is maintained for more than 5 hr.

Other modifications, desirable but not essential, are now under way. They will improve the stirring by redirecting the impulse current and by doubling the stirring capacity. The cooling coil will be removed from the corner near the stirrers and extended around the inner wall of the working area. Finally, a drain of larger diameter will be provided, in order to permit the temperature of the bath to be changed with minimum loss of time.

New equipment acquired during the year included two potentiometer facilities, each consisting of a new design of highly accurate potentiometer with built-in working cell, null instrument, and standard cell of the unsaturated variety. One of these new instruments is seen in figure 3. The potentiometer can be read directly and easily to 10  $\mu$ V or better. The unsaturated standard cells will not be used as primary standards, however, and for this purpose two temperature-controlled laboratory standard units were acquired. Each contains four saturated standard cells mounted in a box and maintained at a constant temperature by electrical means.

A commercial conductivity bridge of intermediate accuracy but high convenience was purchased for use in performing conductivity titrations. For the expanding studies in nonaqueous solvents, the routine rapid measurement of dielectric constants will be necessary. For this purpose, a new instrument has been purchased, together with cells suitable for the dielectric constant range 2 to 90. It is planned to acquire another cell which will extend the range of this instrument to 200 provided suitable standards can be found.

The new laboratories at Gaithersburg are proving, as expected, to be fundamentally well designed and well adapted to the conduct of the Section's operations. Some modifications were inevitable, and most of these have been completed during the current reporting year. Wall cabinets, badly needed in the laboratories but not installed when the building was new, were acquired gradually and put in place. Drain lines were run to connect with the constant-temperature thermostats which are an integral part of the emf equipment.

#### B. Plans and Needs

In general, one of the five emf laboratories in the Section is devoted to studies of aqueous solutions and to pH standardization, while the others will be devoted to the investigation of nonaqueous and mixed solvents, when additional trained personnel to conduct these projects can be found. Needed to complete this unit is an automatic data read-out center which would record automatically and simultaneously the emf of all cells under study in any or all of the five laboratory rooms. Multichannel digital voltmeters of the required accuracy (10  $\mu$ V up to 1.1 V) are now available commercially. The data produced would be programmed for computer analysis, and a permanent record of the emf values would be filed. At the present time, a

more elaborate automated system capable of programming temperature changes, monitoring the approach of the cells to equilibrium and recording the barometric pressure, does not appear practical.

During the past year, the need for developing competence in the area of ion-specific electrodes has been increasingly felt. This project should include glass electrodes, the potentialities of which are far from being exhausted. For studies of these high-impedance systems, a precision high-impedance electrometer of the vibrating-reed type will be needed. As the work progresses, it is likely that time constants of the electrode response will need to be measured, and for this purpose an oscilloscope and electrometer of rapid response will have to be acquired.

As noted in our last report [1], there is a continuing need for methods for the accurate measurement of pH at high temperatures and pressures. No standards of reference for temperatures above 95 °C are available at the present time. Construction of equipment for precise emf measurements of solutions under pressure in the range 100 to 200 °C can only be undertaken when a scientist to undertake this project has been found.

(R. G. Bates)

## 2. MEASUREMENT OF ACIDITY

### A. Concepts and Program

The concept of the Section's programs on the measurement of acidity was set forth in detail in the annual progress report for 1966 [1] and will not be repeated here.

A few remarks concerning the essentially dynamic nature of the national pH scale are perhaps in order. According to the NBS approach, the pH is defined in terms of five primary standards [2]. In the long-term view, however, these standard reference values of pH may be improved and altered as better experimental measurements are obtained. Furthermore, a search is continually underway for new standard reference materials of improved properties, greater stability, and enhanced usefulness. For example, solutions of potassium hydrogen tartrate, one of the present standards, are subject to molding and may be useless for standardization purposes 24 hr after preparation. Potassium hydrogen phthalate, in most respects an excellent standard and widely used, is nevertheless unstable in contact with platinum-hydrogen electrodes. For these reasons, two new promising standard reference materials for the pH range 3.5 to 4.7 are under consideration. These are sodium hydrogen succinate and potassium dihydrogen citrate.

In establishing acidity scales for nonaqueous and mixed solvents, the same concepts are applicable. In addition, management of the programs for acidity in nonaqueous media requires the selection of the most important solvents for study. At the present time priorities are assigned after consideration of a) the extent to which a particular solvent or solvent mixture is used in science and industry. This decision is based on observations of published work and on personal inquiries,

b), the compatibility of a solvent system with the electro-metric pH techniques used almost universally for acidity measurement, and c) the utility of the precise tools for standardization in each particular medium. The NBS standardization procedure relates acidity as directly as possible to the hydrogen electrode potential. If this electrode cannot be used in a particular solvent, the validity of any standard scale is impaired to some degree.

By far the largest number of pH measurements are made in media that are nominally aqueous. Some of these media are of special importance and, due to their fixed composition with respect to predominant solutes, may be considered to advantage as discrete solvent systems. In this category fall sea water, blood plasma, and certain concentrated salt media used widely in the study of the stabilities of metal complexes. When a measurement problem of sufficient magnitude exists in a medium of this sort, it is the NBS policy to establish standards for these particular media of special importance. At the present time a need appears to exist for reference standards in blood plasma (or isotonic saline) and in synthetic or natural sea water.

Current procedures for nonaqueous and partially aqueous solvents lead to the establishment of an acidity scale based on the unit  $\text{pH}^*$  [3]. This is a conventional activity unit referred to a different standard state in each solvent. Hence, it cannot provide the intercomparison of acidities in two or more solvents that has long been sought. This general scale of pH will only become a reality when an acceptable scale of ionic medium effects has been set up [4]. Medium effects for individual ionic species cannot be derived by thermodynamic means. Nevertheless, there is a strong belief that the medium effect (or the related ionic transfer energy) is a real and useful physical concept.

There is some hope that a valid procedure may be found to separate medium effects for electrolytes into their cation and anion constituent parts or to calculate from theory the ionic transfer energy of a single reference ion. Success in this venture would bring to reality the generalized acidity scale envisioned by Brønsted [5]. Consequently, medium effects continue to claim the interest and attention of members of the Section.

(R. G. Bates)

#### B. pH Standards: Sodium Hydrogen Succinate

In spite of its extremely wide use as a pH standard, potassium hydrogen phthalate is not an ideal material for this purpose. The most suitable standard for acidity measurements should be stable in contact with the electrode formed by hydrogen gas adsorbed on platinum, as phthalate buffers are not. Furthermore, reference solutions for pH are useful not only in the standardization of electrometric assemblies but also in the preparation of indicator standards for optical (colorimetric) measurements of pH. Although potassium hydrogen phthalate can be used without difficulty in the visible region of the spectrum, it absorbs strongly in the ultraviolet region and consequently is unsuitable for many spectrophotometric studies of acid-base behavior including the optical method for the determination of dissociation constants.

As a useful alternative to the phthalate standard, our attention has fixed on sodium hydrogen succinate and on potassium dihydrogen citrate, both of which are free from the disadvantages encountered in the use of phthalate solutions. No concentrated effort has yet been devoted to either of these materials. However, some time was spent during the past year (before the loss of V. E. Bower by

transfer to the Electricity Division) in attempts to prepare a sample of sodium hydrogen succinate with the proper stoichiometric composition. For reasons not clearly apparent, these were not very successful. When pure succinic acid and disodium succinate were combined in the proper proportions and the mixture crystallized, the salt obtained did not have the expected composition, within the desired close tolerances. Equipment used for electrometric titrations of this sort is shown in figure 4.



Figure 4. Assembly of equipment for electrometric titrations.

Nevertheless, one series of emf measurements was made with an equimolar mixture of succinic acid and disodium succinate from 0 to 25 °C at intervals of five degrees C. Four cells were included in the series. In each the molality of (synthetic) sodium hydrogen succinate was 0.02 mol kg<sup>-1</sup>, while the molality of added potassium chloride

was 0.015 or 0.01. The emf displayed the expected high stability over a period of 36 hr, with good agreement between the initial and final emf at 25 °C (see table 1). The study of succinate mixtures was, however, discontinued at this point until further attempts to prepare a suitable lot of the acid salt should prove successful.

Table 1. Stability of cells of the type Pt;H<sub>2</sub>, NaHSuc (0.02m), KCl (m), AgCl;Ag.

	m(KCl) = 0.015		m (KCl) = 0.01	
Initial emf (V, 25 °C)	0.60090	0.60113	0.58321	0.58327
Final emf (V, 25 °C)	0.60100	0.60115	0.58316	0.58330

(R. G. Bates)

C. pH\* Standardization: Status of Acidity Standards for Alcohol-Water Media

In the past several years, considerable attention has been given to acid-base behavior in 50 wt percent aqueous methanol. In a paper published early in 1965 [6], reference buffer solutions for pH\* measurements in 50 percent methanol from 10 to 40 °C were proposed. These solutions consisted of acetate buffers, solutions of sodium hydrogen succinate, and phosphate buffers, all of which contained added sodium chloride, necessary for the proper functioning of the silver-silver chloride electrode. The  $p_{a_H}^*$  values of three useful reference standards for acidity measurements in 50 percent methanol are given in table 2.

Table 2. Standard values of  $\text{pH}^*(\text{S})$  in 50 wt percent methanol.

t, °C	HAc (0.02m) NaAc (0.02m) NaCl (0.02m)	NaHSuc (0.02m) NaCl (0.02m)	$\text{KH}_2\text{PO}_4$ (0.02m) $\text{Na}_2\text{HPO}_4$ (0.02m) NaCl (0.02m)
10	5.56	5.81	7.94
15	5.55	5.79	7.92
20	5.54	5.77	7.90
25	5.54	5.76	7.88
30	5.54	5.75	7.87
35	5.54	5.74	7.86
40	5.55	5.74	7.86

Ac = acetate

Suc = succinate

These solutions are useful for standardizing an operational scale of  $\text{pH}^*$  in this solvent medium. For this purpose, the values of  $\text{p}a_{\text{H}}^*$  are identified with  $\text{pH}^*(\text{S})$  in the operational definition

$$\text{pH}^*(\text{X}) = \text{pH}^*(\text{S}) + \frac{E_{\text{X}} - E_{\text{S}}}{(RT \ln 10)/F} \quad (1)$$

In subsequent work,  $p_{a_H}^*$  values were also assigned to two buffer solutions of a different charge type. These solutions consisted of a weak base, tris(hydroxymethyl)-aminomethane ("tris") or 4-aminopyridine, and its corresponding hydrochloride. When pH cells of the glass electrode type were standardized with the first series of buffer standards, measurements of the tris buffers showed that internal inconsistencies existed among the two sets of standards. Even in the aqueous medium there is some evidence that the liquid-junction potential between a concentrated solution of potassium chloride and buffer solutions of weak base-salt type may differ appreciably from that existing in the cell containing standard buffers of the weak acid-salt type [7].

It is evident that the 50 percent methanol solvent system requires further study before the accuracy of practical pH measurements in this medium can approach that obtainable in aqueous solutions. The nature of the abnormality in liquid-junction potentials needs further investigation. In addition, the acetate, succinate, and phosphate standards should be studied with varying concentrations of added chloride, in such a way that the  $p_{a_H}^*$  values in the total absence of chloride can be obtained. For standardization purposes, the addition of chloride to the buffer solution is an inconvenience that should be avoided if possible. When these studies have been successfully completed, suitable standard reference materials will be acquired and certified for issuance.

In view of its wide usefulness as a solvent in acid-base studies, 95 percent ethanol has been chosen as the next solvent system for investigation. The preparation of highly pure and well-characterized solvent is under study and the measurement of ion-pair constants in this medium by conductance methods will be initiated shortly.

(R. G. Bates)

#### D. pD Standards

##### 1. Present Status

The annual progress reports for the past two years [1,8] have summarized all of the experimental work, completed to this time, that has been directed specifically toward the development of standard reference solutions for the measurement of acidity in deuterium oxide. During the past year, the major thrust in the heavy water studies has been an examination of the response of the glass electrode to deuterium ion. This work is described in some detail in section 2.a of this report. A knowledge of the behavior of the glass electrode in heavy water is an essential prerequisite to the drafting of procedures suitable for accurate measurements of pD in practice.

Thus far, conventional  $p_{a_D}$  values have been assigned to three series of solutions in heavy water, namely deuterium chloride [9], a buffer mixture of potassium dideuterium phosphate and disodium deuterium phosphate [10], and an acetate buffer composed of acetic acid ( $CH_3COOD$ ) and sodium acetate [11]. The  $p_{a_D}$  values for one selected solution in two of these three series are listed in table 3, and the solution compositions appear at the foot of the table. The details of the assignment procedures and the nature of the convention used are set forth in the original publications cited above.

Table 3. Standard reference values of  $p_{a_D}$  for an acetate buffer solution and a phosphate buffer solution in deuterium oxide from 5 to 50 °C.

t, °C	Acetate solution	Phosphate solution
5	5.27	7.54
10	5.25	7.50
15	5.24	7.47
20	5.24	7.45
25	5.23	7.43
30	5.23	7.41
35	5.22	7.40
40	5.23	7.39
45	5.23	7.38
50	5.24	7.38

Compositions (in mol kg<sup>-1</sup>):

Acetate solution--CH<sub>3</sub>COOD (0.05), CH<sub>3</sub>COON<sub>a</sub> (0.05)

Phosphate solution--KD<sub>2</sub>PO<sub>4</sub> (0.025), Na<sub>2</sub>DPO<sub>4</sub> (0.025)

It is well known that a solution of a strong acid is not a good reference for standardizing pH cells with liquid junction. Similarly, the solution of deuterium chloride in deuterium oxide, when brought into contact with a concentrated aqueous solution of potassium chloride, displays an abnormal liquid-junction potential relative to that found for buffer mixtures in the same solvent medium.

Nevertheless, the two solutions for which  $p_{a_D}$  values appear in table 3 are quite satisfactory as reference solutions. The phosphate mixture is readily prepared from potassium dihydrogen phosphate and disodium hydrogen phosphate, both of which are already available as NBS Standard Reference Materials. The contamination of the heavy water solvent by the exchanged hydrogen when this solution is prepared is slight and usually of little consequence. For example, the deuterium isotopic composition is reduced by 0.075 percent when the two phosphates are each present at a molality of  $0.025 \text{ mol kg}^{-1}$ .

Unfortunately, the acetate buffer solution is not easy to prepare. The best procedure is probably to add sodium carbonate in the proper amount to a solution prepared by dissolving a weighed quantity of pure acetic acid in heavy water. Both materials are hygroscopic and difficult to weigh accurately in the small quantities usually required. The issuance of acetic acid as a standard reference material does not appear feasible at the present time.

For the most useful standardization of a practical  $p_D$  scale, therefore, other buffer systems should be studied. To replace acetate at the lower end of the  $p_D$  scale, succinate and citrate buffers are likely possibilities. For the upper end, a carbonate buffer solution shows promise of usefulness. Contamination of the solvent with hydrogen would be minimal with sodium hydrogen succinate and a buffer solution composed of sodium bicarbonate and sodium carbonate, as only one atom of hydrogen is contained in molal amounts of these buffer systems. Potassium dihydrogen citrate would be slightly less suitable in this respect, but its other favorable characteristics warrant its further study. For example, the buffer capacity of solutions of primary citrate salts exceeds that of acid succinates at the same

molal concentration. Furthermore, potassium dihydrogen citrate has a considerably lower pD than does sodium hydrogen succinate when these salts are dissolved at the same concentration in deuterium oxide. Both salts appear suitable for issuance as well-characterized standard reference materials.

When the  $p_{a_D}$  values of two or more suitable reference solutions have been obtained by means of emf measurements of cells without liquid junction, they can be identified with pD(S) in an operational definition of the practical pD scale:

$$pD(X) = pD(S) + \frac{E_X - E_S}{(RT \ln 10)/F} \quad (2)$$

The usefulness of this practical scale will, however, depend on the purity of the response of the glass electrode to deuterium ion and on the regularity of the liquid junction potential between solutions (X) and (S) in heavy water and the concentrated aqueous solution of potassium chloride with which they make contact at the liquid junction. These are factors which will require further study.

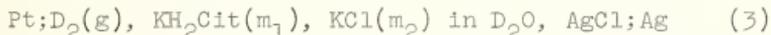
(R. G. Bates)

## 2. Potassium Dihydrogen Citrate

In a continuation of the program of selection and certification of standard reference materials for pD measurements, potassium dihydrogen citrate was selected as the next material to be studied. At the present time two buffer mixtures, one containing potassium dideuterium phosphate and disodium deuterium phosphate and the other containing acetic acid and sodium acetate, have already been proposed as primary buffer standards in heavy water.

However, the second buffer mixture is rather inconvenient to prepare. It would therefore be preferable to use potassium dihydrogen citrate, which is a solid material and can be prepared and purified with relative ease. In solution this salt is converted, by exchange with the heavy water, into potassium dideuterium citrate, and its solutions in heavy water exhibit a pD value near 4.5.

a. Method. The standard values of  $pa_D$  for the newly selected buffer material will be derived by a method which follows closely the usual NBS procedure for establishing primary pH standards in ordinary water. The acidity function  $p(a_D\gamma_{Cl})$  for a particular buffer concentration with different amounts of added soluble chloride will be determined by measuring the emf of the cell



over a range of temperatures. The measured emf ( $E$ ), the standard emf ( $E^\circ$ ), and natural constants are then used in the computation of acidity functions  $p(a_D\gamma_{Cl})$ . The function  $p(a_D\gamma_{Cl})^\circ$  is evaluated by extrapolating the values of  $p(a_D\gamma_{Cl})$  to zero concentration of the added chloride.

The  $pa_D$  values are derived by means of the equation

$$pa_D = p(a_D\gamma_{Cl})^\circ + \log \gamma_{Cl} \quad (4)$$

where the ionic activity coefficient of chloride ion is estimated by the use of the Bates-Guggenheim convention [12]

$$-\log \gamma_{Cl} = \frac{AI^{1/2}}{1+1.5I^{1/2}} \quad (5)$$

In eq 5, A is a constant of the Debye-Hückel theory, the magnitude of which reflects the dielectric constant and density of the heavy water solvent, and I is the ionic strength.

b. Experimental. The potassium dihydrogen citrate was prepared according to the directions of Kolthoff [13]. Citric acid was neutralized with a calculated amount of potassium carbonate to yield the desired primary salt. Two lots of potassium dihydrogen citrate were prepared by this method. They were assayed by weight titration with a standard solution of sodium hydroxide which itself had been standardized against a standard solution of distilled hydrochloric acid. The endpoint of the titration was determined potentiometrically. The first lot assayed 100.01 percent (standard deviation 0.04 percent) and the second lot gave 100.03 percent (standard deviation 0.03 percent), indicating that the material was sufficiently pure for further study. A few emf measurements of cell 3 have been made in order to select the most suitable concentration for the proposed reference solution.

(Mays Paabo)

#### E. Measurement of Acidity in Biological Media

There is an increasing awareness of the role that the Analytical Chemistry Division can, and should, play in improving the measurements on which the success of biomedical research and the accuracy of clinical diagnoses depend. Likewise, the Section is gradually becoming more deeply involved in the special problems encountered in the measurement of the acidity of biological media.

Some years ago, a standard reference phosphate buffer for pH measurements of blood was established [14]. This work was undertaken to meet the needs of clinical chemists

and research workers for a standard solution of pH about 7.4 at 37 °C which would facilitate the discrimination of pH differences in blood with an accuracy greater than 0.01 unit. This standard is widely used.

Three conferences of the New York Academy of Sciences have served to strengthen the lines of communication between the NBS specialists in pH and research workers in biomedicine. The first took place in December 1960 and was entitled "In Vitro and In Vivo Effects of Amine Buffers" (see reference [15]), while the second, entitled "Current Concepts of Acid-Base Measurement", was held in November 1964. The third, devoted to the subject "Bioelectrodes", took place in June 1966. The chief of the Section was an invited speaker at all three of these meetings. Reprint requests for the second of these lectures [16] have exceeded 350 and are still being received. As an outgrowth of this conference, R. G. Bates was asked to serve as a member of two ad hoc committees, one dealing with acid-base terminology and the other with methodology. The committee reports have been published [17]. The proceedings of the third conference have not yet appeared.

A comparatively recent development in the electrochemical investigation of biological systems is the glass microelectrode. These electrodes are of both the open- and closed-tip designs, and the tip diameters may be as small as 0.1  $\mu\text{m}$ . They have been used successfully to measure pH and cation concentrations as well as membrane potentials. An illuminating conference devoted to intracellular glass electrodes was held at the University of Montreal in May 1967, at which the chief of the Section presented an invited lecture on factors determining the choice of inner reference systems for these electrodes. He has likewise been invited to be a co-author of a review article on micro-

electrodes, the major portion of which is being compiled by Drs. Butler, Waddell, and Poole of the Medical School, University of North Carolina.

These conferences, together with a visit to the glass-electrode facility of the Corning Glass Works in the spring of 1967, have produced suggestions for new standard reference materials capable of enhancing the reliability of clinical and research data. One proposal is for the establishment of a standard with the same pH, ionic strength, sodium ion concentration, and protein concentration as blood plasma. Another proposal is for a pH standard in isotonic saline. These suggestions are both meritorious and feasible, and it is hoped that they can be incorporated into the Section's programs in the near future.

(R. G. Bates)

#### F. Measurement of Acidity in Sea Water

Growing interest in the study of the oceans demands that techniques be developed for accurately determining the hydrogen ion concentration or activity in the seas. In the interest of serving the research community, the NBS has set out to develop pH standards for media approximating sea water in composition. These standards would be made available through the Standard Reference Materials program, as are the present materials for standardizing pH equipment for general use. To achieve this goal, data must be accumulated on the effect of sea water on the activity of hydrogen ion and on the response of pH electrodes.

The initial phase of this work is being performed in collaboration with James T. Clark and Dr. Donald Rosenthal of Clarkson College of Technology. A chloride solution has been prepared which simulates the composition of natural sea water. The composition of this simulated synthetic sea water (SSW) is as follows:

NaCl	0.4158 mol kg <sup>-1</sup>
MgCl <sub>2</sub>	0.05417
CaCl <sub>2</sub>	0.01034
KCl	0.00923
SrCl <sub>2</sub>	0.000158

The ionic strength of the SSW is varied by dilution. This composition is similar to that of Lyman and Fleming's formula for 19% chlorinity sea water [18].

The emf is being determined over the temperature range 5 to 45 °C for dilute solutions of hydrochloric acid in SSW, and in diluted concentrated solutions of similar relative composition, using the cell with a hydrogen electrode

and a silver-silver chloride electrode. The following molal concentrations of hydrochloric acid are being studied: 0.005, 0.01, 0.033, 0.066, and 0.10. The acidity function  $p_{a_H} \gamma_{Cl^-}$  [that is,  $-\log(a_{H^+} \gamma_{Cl^-})$ ] is derived from the measured emf and the known concentrations, and its variation with the chloride concentration is being studied.

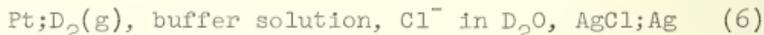
Thus far information has been obtained for most of the chloride and HCl concentrations. Repeat determinations must be run in several cases to check on the reproducibility of the emf measurements. In addition, some of the solutions have yet to be measured. In all, approximately 50 percent of the experimental work has been completed.

In addition to the above study with the hydrogen-silver chloride cell without liquid junction, a similar study with the glass-calomel system is to be undertaken. This will involve measuring the glass electrode pH in these same solutions of HCl-SSW in order to measure the effect of salt concentration on the potentials of the glass electrode.

(J. T. Clark, Jr.)

#### G. Behavior of Glass Electrodes in Deuterium Oxide

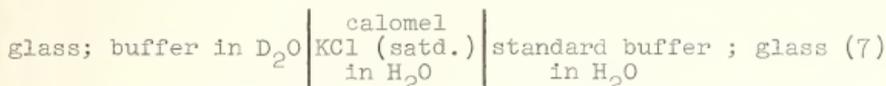
It is a common practice to use commercial glass electrodes for measurements of acidity in water, in many nonaqueous solvents, and also in deuterium oxide. Various workers have found that in order to obtain pD from the operational pH value, referred to the usual pH standards prepared in ordinary water, an empirical correction of 0.40 pH unit should be added to the pH meter reading [19,20]. Recently, however, a pD scale based on conventional values of  $p_{aD}$  in certain buffer solutions has been established through measurements of the emf of the cell [10,11]



Phosphate and acetate buffer solutions were used in the work. To examine the experimental basis for a practical scale of pD, a study designed to affirm the deuterium response of the glass electrode and the validity of the empirical correction factor was undertaken [1]. Glass electrodes were compared both directly and indirectly against deuterium gas electrodes in buffered solutions covering a range of 12 pD units.

## 1. Method

The experimental procedures consisted of two major parts. First, the behavior of several glass electrodes from different manufacturers was observed in buffer solutions in heavy water after the glass electrodes had been standardized in a buffer solution made up in ordinary water. A saturated aqueous calomel electrode was used as the reference electrode. The cell can be represented by

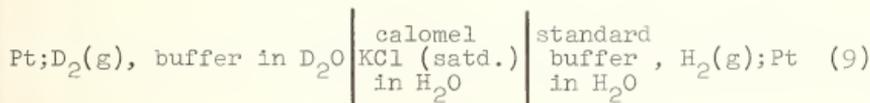


The apparent pD can be calculated from the emf (E) of this cell by the following equation:

$$\text{pD (apparent)} = \text{pH(S)} + \frac{E_X - E_S}{(RT \ln 10)/F} \quad (8)$$

where  $E_S$  and  $E_X$  are values of emf of the cell when the glass electrode is immersed in the standard or in the "unknown" buffer solution in heavy water, respectively, each half cell being measured against the calomel reference electrode. The pH(S) is the assigned value of the standard solution on a conventional activity scale in water.

Measurements were also made of the same type of cell in which the glass electrodes were replaced by deuterium or hydrogen gas electrodes:

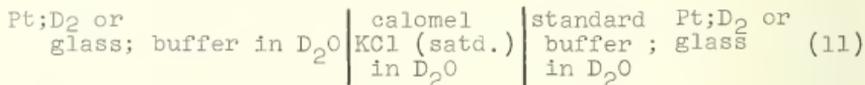


The apparent pD values obtained from measurements of these two cells with liquid junction were then compared with the

corresponding  $p_{aD}$  values obtained from measurements of cell 6 containing the same buffer solutions in heavy water as did cells 7 and 9. The empirical correction factor  $\delta_{app}$  results from a comparison of  $p_{aD}$  with the apparent  $pD$  derived from the emf of the cells with liquid junction:

$$\delta_{app} = p_{aD} - pD \text{ (apparent)} \quad (10)$$

In the second procedure, the behavior of glass electrodes in heavy water was observed after these electrodes had been standardized in a reference buffer solution prepared in heavy water. The cell with liquid junction used contained a saturated calomel electrode also made up in heavy water. This cell avoids the differences in liquid junction potential between two different solvents. It can be represented by



The operational  $pD$  furnished by this cell will be designated  $pD$  to distinguish it from  $pD$  (apparent) found when standards in ordinary water were used and the bridge solution consisted of saturated KCl in ordinary water:

$$pD = pD(S) + \frac{E_X - E_S}{(RT \ln 10)/F} \quad (12)$$

Again  $E_X$  and  $E_S$  are the emf values of the left and right half cells measured against the calomel reference electrode.

By combining the values of  $pD$  and the  $pa_D$  derived from independent measurements of cells without liquid junction, correction factors were obtained for both glass and gas electrodes:

$$\delta = pa_D - pD \quad (13)$$

Finally, in addition to the indirect comparisons of the glass electrodes with deuterium gas electrodes as outlined above, a direct comparison was made by means of the following cell:



## 2. Experimental

The heavy water used was of high isotopic purity (about 99.75 percent). Measurements of the emf of cells with glass electrodes were made on a commercial pH electrometer of the battery type. Systems of low electrical resistance were measured with a precision potentiometer. The electrometer and other associated measuring equipment are shown in figure 5. All measurements were performed at 25 °C. The buffer systems selected for study covered the  $pD$  range from 1 to 13. Preparation of the solutions, electrodes, and cells followed the usual procedures of the Section. Two of the cell vessels used for the study of glass electrodes are illustrated in figures 6 and 7.

## 3. Results

The operational correction factors for six of the buffer systems studied have been calculated and are given in table 4. It is evident that the correction factors which need to be applied to  $pD$  measurements based on pH standards in ordinary water are constant but differ in magnitude for glass and gas electrodes. The correction appears to be nearly zero when the glass electrode is

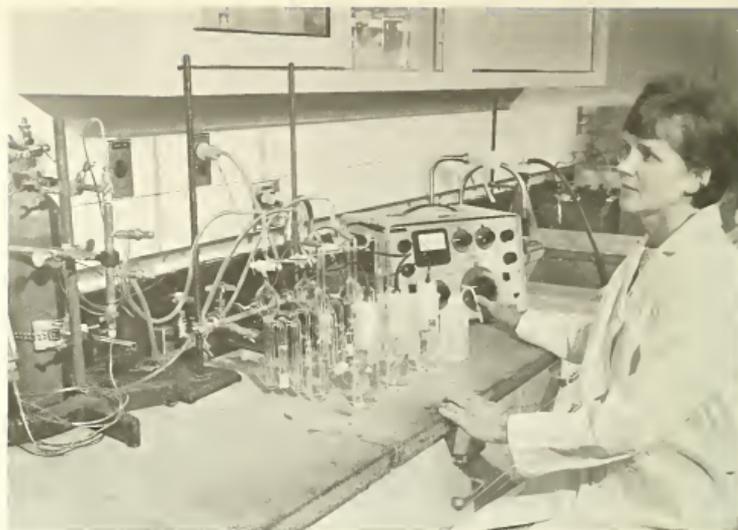


Figure 5. Assembly of apparatus for studies of the behavior of glass electrodes in heavy water.

Table 4. Correction factors for operational pD measurements in heavy water solutions.

Buffer	Standard buffer and reference electrode in H <sub>2</sub> O		Standard buffer and reference electrode in D <sub>2</sub> O	
	$\delta_{app}$ (gas)	$\delta_{app}$ (glass)	$\delta$ (gas)	$\delta$ (glass)
Citric acid	+0.067	+0.470	+0.003	-0.001
D <sub>2</sub> Suc, NaDSuc	+0.068	+0.466	-0.001	-0.018
DAc NaAc	+0.077	+0.460	+0.009	-0.002
Borax	+0.078	+0.472	+0.016	+0.034
NaDCO <sub>3</sub> , Na <sub>2</sub> CO <sub>3</sub>	+0.079	+0.459	+0.007	+0.043

Suc = succinate  
Ac = acetate

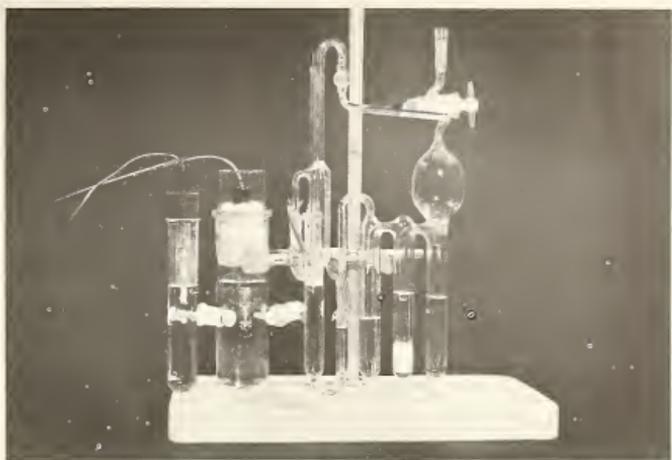


Figure 6. Emf cell used for the direct and indirect comparison of glass electrodes with the deuterium gas electrode in heavy water.

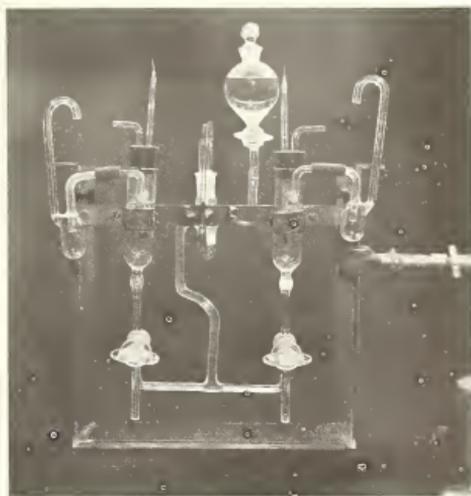


Figure 7. Emf cell with liquid junction, containing a calomel electrode prepared with heavy water.

standardized in a reference buffer solution prepared in heavy water. The direct comparison of two of the glass electrodes with the deuterium gas electrode is illustrated in figure 8. These glass electrodes follow the potential of the deuterium gas electrode within 0.5 mV over most of the pD range studied. There is evidence, however, that some glass electrodes show greater alkaline errors than would be expected in the corresponding aqueous solutions.

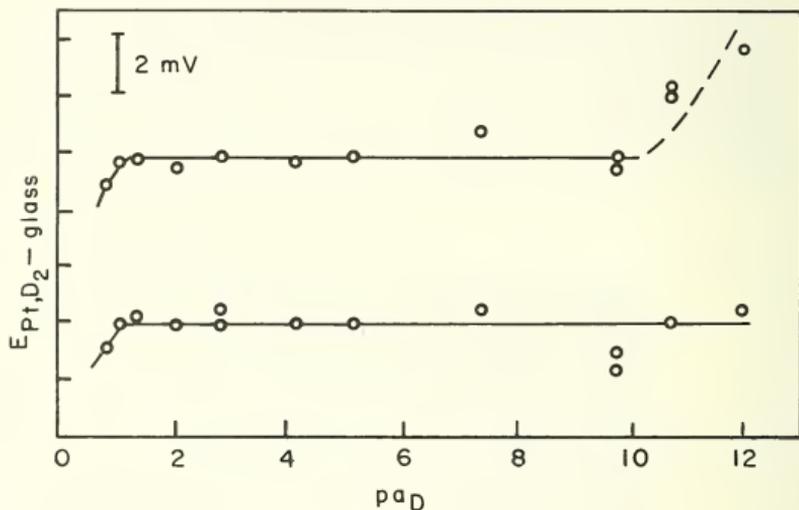


Figure 8. Direct comparison of two glass electrodes with the deuterium gas electrode over a range of pD.

(Maya Paabo)

### 3. SOLVENT EFFECTS ON IONIC PROCESSES

#### A. Ion-Solvent Interactions

As solvent effects on the equilibrium behavior of strong and weak electrolytes are examined in ever greater detail, it becomes increasingly evident that electrostatic effects related to the changing dielectric constant of the medium cannot account for the observed changes. The electrostatic treatment alone is moderately successful in amphiprotic hydrogen-bonding media of relatively high dielectric constant. At the other extreme, in aprotic solvents of low dielectric constant, other factors play a dominant role. The properties of solvents--dielectric constant, hydrogen-bonding capacity, basicity, and solvating power, for example--vary widely, and consequently all gradations in behavior may be expected and are indeed found in practice.

A convenient way of examining the solvent effect on an ionic process involving two or more species is through the transfer free energy  $\Delta G_t^\circ$ , namely the free energy change for the transfer

$$i \text{ (in water, } w) = i \text{ (in solvent } s)$$

between the standard states in the solvents  $w$  and  $s$ :

$$\Delta G_t^\circ = {}_s G^\circ(i) - {}_w G^\circ(i) \quad (15)$$

Another useful quantity for comparison purposes is the "medium effect"  ${}_m \gamma_i$  or "medium activity coefficient", which is simply related to the free energy of transfer [21]:

$$\log {}_m \gamma_i = \Delta G_t^\circ / (RT \ln 10) \quad (16)$$

Transfer free energies and medium effects for uncharged species, for neutral combinations of ions, and for certain other ionic combinations can be obtained with full thermodynamic rigor by experimental means. If the transfer energy for any single ionic species could be measured or calculated, these combinations would permit a scale of medium effects for all ions to be set up. So far this is not possible. Nevertheless, differences in the medium effect for two ionic species are often revealing, and information of this sort can often be derived from measurements of solvent effects on equilibrium constants such as the dissociation constants of weak acids.

In this way, it has been possible to identify several influences of qualitative significance. The increased free energy of an ion as the dielectric constant decreases has long been recognized and is given semi-quantitative expression through the Born equation [22]. The relationship between dielectric constant and the formation of ion pairs has also been elucidated [23]. When the hydrogen-bonding capacity of the solvent is markedly reduced, an entirely different group of interactions may become important [24]. The efforts of the conjugate bases of protonated species HA and  $BH^+$  to achieve stability may lead to the formation of the homoconjugates  $AHA^-$  and  $EHB^+$ , to analogous heteroconjugates, and to higher aggregates (see, for example, references [25] and [26]. Anions such as picrate and other phenolates which are "delocalized oscillators" may interact particularly strongly with solvent molecules through enhanced dispersion forces [27].

It is quite evident that an understanding of ion-solvent interactions would provide the key to an explanation of the many diverse aspects of what are known as solvent effects.

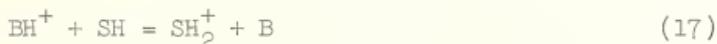
Furthermore, scales of ionic medium effects, whether based on experiment or theory, would provide the basis not only for a single scale of electrode potentials but for a single "universal" acidity scale.

For these reasons, ion-solvent interactions provide a unifying theme for a large part of the research activity of the Section. This subject is of interest here not only from the equilibrium point of view but also in the study of transport processes such as conductance and diffusion. It is believed that progress in this area is an essential prerequisite to advancements in the electrochemistry of nonaqueous media.

(R. G. Bates)

#### B. Medium Effects for Chlorides in Methanol-Water Solvents

Solvent effects on the acidic dissociation of positively-charged weak acids were discussed in some detail in the annual progress report for 1966 [1]. This process can be written in general terms as follows



where B represents an uncharged base such as ammonia or tris(hydroxymethyl)aminomethane ("tris", THAM). A Guest Worker in the Section, Professor Paul W. Schindler, studied the dissociation of tris in methanol-water solvents with compositions ranging from 30 to 90 wt percent methanol and determined the solubility of the base over the entire composition range from 0 to 100 percent methanol at 15, 25, and 35 °C. These data, together with results in the literature for the energies of transfer of hydrochloric acid and the alkali chlorides, from water to water-methanol solvents,

have made it possible to account for the minimum in the  $p_K$  of protonated tris and ammonium ion as methanol is added to the aqueous solvent. A manuscript on this subject has been prepared for publication.

The difference between  $p_s K$  in the methanol-water mixture and  $p_w K$  in the aqueous medium depends on a combination of the medium effects  ${}_m \gamma_i$  for the species participating in the dissociation process. For the dissociation of  $\text{tris} \cdot \text{H}^+$  (designated  $\text{TH}^+$ ),

$$p_s K - p_w K = \log {}_m \gamma_T + \log {}_m \gamma_{\text{H}^+} - \log {}_m \gamma_{\text{TH}^+} \quad (18)$$

which may also be written in terms of the mean medium effects for the two chlorides  $\text{HCl}$  and  $\text{THCl}$ :

$$p_s K - p_w K = {}_m \gamma_T + 2 \log {}_m \gamma_{\text{HCl}} - 2 \log {}_m \gamma_{\text{THCl}} \quad (19)$$

Inasmuch as medium effects for individual ions in a given solvent medium are, by definition, completely independent of other counter ions, an equation analogous to eq 19 could be written for bromides, iodides, perchlorates, and so on.

The solubility measurements permit reasonably accurate values for  ${}_m \gamma_T$  to be obtained, and  ${}_m \gamma_{\text{HCl}}$  is known with considerable precision from extensive measurements of the standard emf of cells with hydrogen electrodes and silver-silver chloride electrodes containing hydrochloric acid in methanol-water solvents (see reference [28]). Hence, the measurements of  $p_s K - p_w K$  permit the medium effect for the transfer of tris hydrochloride from water to methanol-water solvents to be calculated by eq 19. The values obtained are compared in table 5 with similar data for lithium chloride and sodium chloride derived from solubility measurements [29].

Table 5. Medium effects for chloride salts in methanol-water solvents at 25 °C.

Wt. percent MeOH	$\log m\gamma_{\text{THCl}}$	$\log m\gamma_{\text{LiCl}}$	$\log m\gamma_{\text{NaCl}}$
30	0.319	0.361	0.492
50	0.563	0.620	0.853
70	0.867	0.936	1.282
90	1.240	1.369	1.870

Although medium effects and ionic transfer energies for individual ionic species are not experimentally obtainable (see next section), eq 18 shows that differences between the logarithms of the medium effects of ions of like charge can be derived unambiguously from measurements of solvent effects on the pK for certain dissociation equilibria. Furthermore, it is evident that similar information can be obtained from medium effects for electrolytes measured by emf, solubility, and other methods. Thus,

$$\log m\gamma_{\text{M}^+} - \log m\gamma_{\text{H}^+} = \log m\gamma_{\text{MX}} - \log m\gamma_{\text{HX}} \quad (20)$$

where  $\text{M}^+$  may be, for example, an alkali ion and  $\text{X}^-$  a halide ion. Figure 9 is a plot of some of these differences calculated from pK measurements and from data given in the literature.

The form of the curves shown in Figure 9 is sufficiently unusual as to require comment. The sharp rise, independent of whether  $\text{M}^+$  (or  $\text{BH}^+$ ) is  $\text{tris}\cdot\text{H}^+$ , ammonium ion, or lithium ion, shows that the transfer energy of the

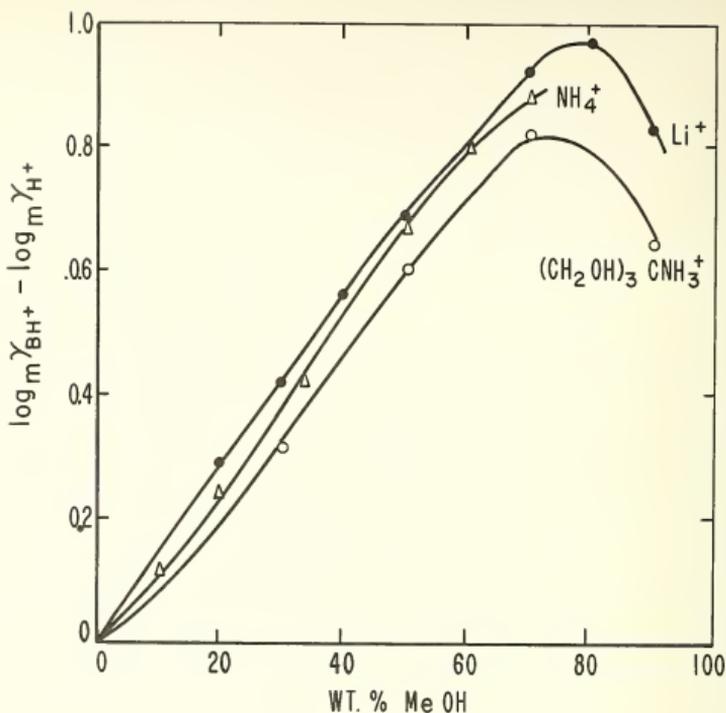


Figure 9. Differences between the medium effects for individual ionic species in methanol-water solvents.

proton is much smaller than those of these three other cations at methanol concentrations from 0 to 70 wt percent. Above 70 wt percent, however, the curves begin to fall off, suggesting that the free energy of the proton in methanol-rich solvents is rising more rapidly than that of the other cations. It is tempting to attribute this observation to a "basicity effect" [30]. In these terms, the basicity of

methanol-water solvents would be greater than water itself in the low range of methanol concentrations but would decrease rapidly as the amount of water in the mixture becomes low. There is no general agreement as to the effective basicity of alcohols and alcohol-water mixtures [31].

(R. G. Bates)

### C. Medium Effects for Individual Ionic Species

The realization of several long-term goals of analytical and physical chemists intimately involved in measurement problems depends on the establishment of a valid and useful scale of medium effects for individual ionic species. Scales of electrode potentials, for example, have been set up in several different solvents, but these values must necessarily always be referred to an arbitrary zero, usually the standard potential of the hydrogen, hydrogen ion couple in each particular solvent under study. Fusion of scales of relative electrode potential into a single unified system would demand a knowledge of the standard hydrogen electrode potential in each of these solvents relative to a single, solvent-independent, reference point. The latter would most conveniently be the standard hydrogen electrode in the aqueous medium. The difference between the potential of the standard hydrogen electrode in a given solvent and that in water is directly related to the transfer free energy and the medium effect for the hydrogen ion (proton):

$${}_wE^\circ(\text{H}) - {}_sE^\circ(\text{H}) = \frac{RT}{F} \ln m \gamma_{\text{H}} \quad (21)$$

Similarly, the standard scales of  $\text{pH}^*$  being established in the Section for mixed solvents and other amphiprotic media are based on conventional values of  $\text{pa}_{\text{H}}^*$  defined in terms of the activity of hydrogen ion related to the standard state in each solvent or solvent mixture:

$$\text{pa}_{\text{H}}^* = -\log (m_{\text{H}} \cdot s_{\text{H}} \gamma_{\text{H}}) \quad (22)$$

Although these scales are capable of furnishing relative values of the acidity of different solutions in the same solvent, they cannot relate the acidities of solutions in different solvent media to a single reference point. The situation is thus analogous to that encountered with electrode potentials. Again it is the medium effect for hydrogen ion or the proton that is needed in order to realize a general  $\text{pa}_{\text{H}}$  scale which would be based on the aqueous standard state regardless of the solvent. Only such a general scale could interrelate the acidity of different solvent media in a valid and useful quantitative fashion:

$$\text{pa}_{\text{H}} = -\log (m_{\text{H}} \cdot s_{\text{H}} \gamma_{\text{H}} \cdot m_{\text{H}} \gamma_{\text{H}}) = \text{pa}_{\text{H}}^* - \log m_{\text{H}} \gamma_{\text{H}} \quad (23)$$

There have been many suggestions for interesting and novel approaches by which the medium effect of a single ionic species might conceivably be evaluated. As we have already indicated, the derivation of the medium effect of one ionic species in each medium is a necessary and sufficient condition for setting up a scale of medium effects for all ions in that medium through the use of experimentally accessible medium effects for ion combinations. Although

many of these proposals are eminently reasonable as well as highly ingenious, the results furnished thus far are in serious disagreement. The variation even extends to the sign of the logarithm of the medium effect, as shown in table 6, where results for the medium effect of hydrogen ion in methanol-water solvents are given.

Table 6. Medium effects ( $\log_m \gamma_H$ ) for the transfer of hydrogen ion from water to methanol-water solvents.

Wt percent MeOH	Izmailov [32]	Feakins, Tomkins [33]	deLigny and Alfenaar [34]
10	-	-0.37	-0.19
43.1	0.35	-2.05	-1.02
50	0.43	-2.37	-
90	1.45	-3.91	-
100	3.3	-	-0.88

It is clear that the Section is intimately concerned with all efforts to establish scales of ionic medium effects and ionic transfer energies. During the past year, considerable effort was devoted to reviewing and evaluating recent progress in this interesting and controversial area. The results of this examination were incorporated in a chapter entitled "Medium Effects and pH in Nonaqueous Solvents" which was prepared for a book Solvation Interactions to be published by Marcel Dekker (J. F. Coetzee and C. D. Ritchie, Eds.). This material also formed the basis for the keynote address to the Symposium on Electrochemistry in Nonaqueous Media at the Dallas meeting of the Electrochemical Society in May.

(R. G. Bates)

#### D. Potentiometric Studies in N-Methylpropionamide

Dawson and his associates [35] have studied N-methylamides, which have high dielectric constants. One of these compounds, N-methylpropionamide, is a liquid stable over a wide temperature range, freezing at  $-40^{\circ}\text{C}$  and giving reproducible dielectric constant and density measurements at temperatures in excess of  $150^{\circ}\text{C}$ . The dielectric constant of the liquid is 176 at  $25^{\circ}\text{C}$ . Furthermore, the liquid amide has remarkable solvent properties, being completely miscible with water and several of the hydrocarbons of low molecular weight. Many organic and inorganic compounds are likewise quite soluble in N-methylpropionamide.

A study of acid-base equilibria and pH measurements in this solvent has been initiated. Accurate and reproducible potentiometric measurements were made of dilute hydrochloric acid solutions at  $25^{\circ}\text{C}$  using a cell consisting of a hydrogen electrode and a silver-silver chloride electrode. Collateral measurements were also made at 10, 40, 55, 85, and  $113.6^{\circ}\text{C}$ . The hydrochloric acid solutions were somewhat unstable at the higher temperatures, and hence the emf data at these temperatures are less accurate than those obtained at  $25^{\circ}\text{C}$ .

The acidity function  $p(a_{\text{H}^+}\gamma_{\text{Cl}^-})$  can be calculated from the emf values, and the standard emf can be derived by an extrapolation procedure. The measurements have been completed, but the analysis of the results is still under way.

(Donald Rosenthal)

## E. Acid-Base Behavior in Aprotic Organic Solvents

Under special arrangement, Dr. Marion Maclean Davis, who left the Section at the end of 1965, devoted the calendar year 1966 to the completion of a comprehensive and important manuscript reviewing the behavior of acids and bases in aprotic solvents. This work will be published as an NBS Monograph in the near future, and a briefer version will appear as a chapter in one of the volumes of The Chemistry of Non-Aqueous Solvents (J. J. Lagowski, Ed.). The scope of the manuscript, which is entitled "Acid-Base Behavior in Aprotic Organic Solvents", is indicated by the following abstract:

"A unified picture of acid-base behavior in aprotic organic solvents is presented, based on an extensive survey of the literature and experimental results of the author and associates. Evidence given to support this picture includes data pertaining to colligative properties of acids, bases, and salts and also conductance, dielectric constants, distribution between immiscible solvents, and spectral absorption in the infrared, visible, and ultraviolet. The solvents emphasized are hydrocarbons and halo-hydrocarbons, but data for dipolar aprotic solvents (for example, acetone, acetonitrile, and nitrobenzene) are included. Contrasts in acid-base behavior and in acidity and basicity scales in aprotic and water-like solvents are discussed.

"The role of hydrogen bonding in aprotic solvents is discussed at length. Important types of hydrogen-bonded structures include chelate rings; self-associated acids, bases, and salts; hydrogen-bonded ion pairs; and homo- and heteroconjugate cations and anions. Examples are given in which hydrogen bonding of these types affects such properties as the absorption spectrum of a salt, the catalytic effect of an acid, and the accurate location of a titration endpoint."

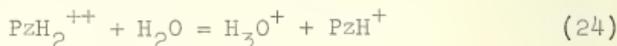
(R. G. Bates)

#### 4. EQUILIBRIUM DATA FOR IONIC SYSTEMS

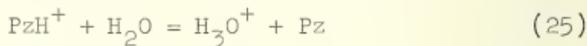
##### A. Dissociation of Piperazinium Ions in Water

As part of a study of heterocyclic nitrogenous bases, the dissociation constant of piperidine,  $C_5H_{10}=NH$ , was measured several years ago in this section [36]. The twofold object of the work was to study the effect of structure on the basicity and other thermodynamic properties of this substance and to look for further useful buffer solutions for pH standardization and control. In a continuation of this work, a study was later made of the dissociation constant of pyrrolidine,  $C_4H_8=NH$ , a compound that differs from piperidine in having a five-membered ring instead of a six-membered ring [37]. More recently, similar studies have been concerned with morpholine,  $O=C_4H_8=NH$ , a compound in which an additional hetero atom is introduced into the piperidine ring [38].

During the past year, work has been completed on piperazine,  $HN=C_4H_8=NH$ , a base that can, on protonation, form two acidic species, namely  $H_2N^+=C_4H_8=NH$  and  $H_2N^+=C_4H_8=N^+H_2$ . The dissociation of these two acids can be represented schematically by



and



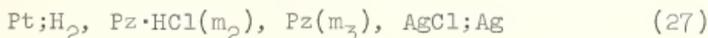
where Pz is written for the neutral base piperazine. Corresponding to these two stages of dissociation, there are two dissociation constants,  $K_1$  and  $K_2$  respectively, and it is therefore possible to study the effect of both the  $NH_2^+$  group and the NH group on the dissociation of the other  $NH_2^+$  group. Both the base and its salts are of

importance as pharmaceuticals, the salts especially being used in veterinary medicine as anthelmintics.

Electromotive force measurements were made, using two cells which can be represented



and



The emf  $E$  of cell 26 is related to the first dissociation constant ( $K_1$ ) of diprotonated piperazine by the equation

$$\begin{aligned} (E-E^\circ)/k + \log m_{\text{Cl}^-} + \log (m_1/m_2) \\ = \text{p}K_1 - \log (\gamma_{\text{PzH}_2^{++}} \cdot \gamma_{\text{Cl}^-} / \gamma_{\text{PzH}^+}) \end{aligned} \quad (28)$$

where  $k$  stands for  $(RT \ln 10)/F$  and  $E^\circ$  is the standard emf of the hydrogen-silver chloride cell in water.

A quantity  $\text{p}K_1'$  can be defined as follows:

$$\text{p}K_1' = (E-E^\circ)/k + \log m_{\text{Cl}^-} + \log (m_1/m_2) - 4AI^{1/2} \quad (29)$$

where  $A$  is the slope parameter of the Debye-Hückel equation. Then the relationship

$$\text{p}K_1' = \text{p}K_1 + bI \quad (30)$$

holds to a good approximation and  $\text{p}K_1$  can be obtained by extrapolating values of  $\text{p}K_1'$  to zero total ionic strength ( $I$ ), using the method least squares. An extrapolation of the data at 25 °C is shown in figure 10.

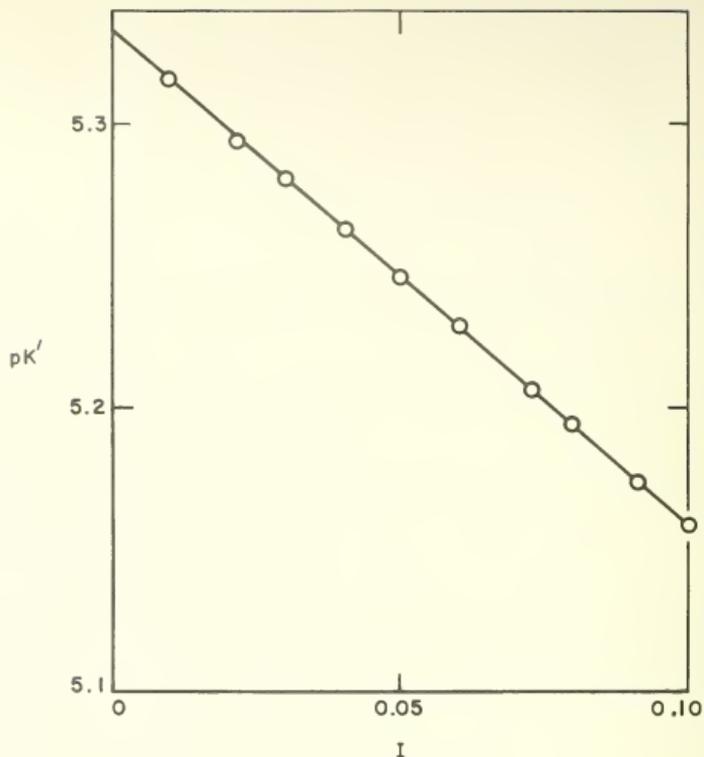


Figure 10. Extrapolation curve for obtaining  $pK_1$  from the values of  $pK'_1$ .

Cell 27 was used for the determination of the second dissociation constant, the equilibrium constant for reaction 25. The emf of this cell is related to  $pK_2$  by the equation

$$\begin{aligned}
 (E-E^\circ)/k + \log m_{Cl^-} + \log (m_2/m_3) \\
 = pK_2 - \log (\gamma_{PzH^+} \cdot \gamma_{Cl^-} / \gamma_{Pz}) \quad (31)
 \end{aligned}$$

A small correction was made to the buffer-ratio term,  $\log (m_2/m_3)$ , because of the slight hydrolysis of the base. The function used to obtain the true value of  $pK_2$  by extrapolation of  $pK_2'$  values to zero ionic strength was, therefore

$$pK_2' = (E - E^\circ)/k + \log m_{Cl^-} + \log \frac{m_2 + m_{OH}}{m_3 - m_{OH}} - 2AI^{1/2} \quad (32)$$

Measurements were made over a range of temperature from 0 to 50 °C. The variation of both  $pK_1$  and  $pK_2$  with temperature is considerable; that for  $pK_1$  is shown in figure 11. Thermodynamic quantities for the dissociation of piperazinium ions and certain of their analogues at 25 °C, derived from emf measurements made in this section, are given in table 7.

Table 7. Comparison of thermodynamic constants for the dissociation of piperazinium, morpholinium, piperidinium, and pyrrolidinium ions at 25 °C.

	pK	$\Delta H^\circ$ J mol <sup>-1</sup>	$\Delta S^\circ$ J deg <sup>-1</sup> mol <sup>-1</sup>	$\Delta C_p^\circ$ J deg <sup>-1</sup> mol <sup>-1</sup>
Piperazinium ion				
First stage	5.333	31,080	+ 2.2	87
Second stage	9.73 <sub>1</sub>	42,870	-42.5	73
Morpholinium ion	8.492	39,030	-31.7	48
Piperidinium ion	11.123	53,390	-33.9	88
Pyrrolidinium	11.305	54,470	-33.7	68

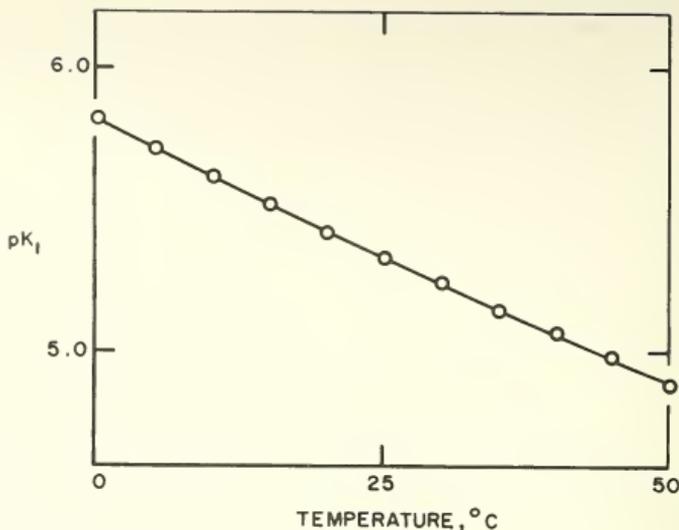


Figure 11. Variation of  $pK_1$  for piperazinium ion with temperature. (Circles are experimental points; the line represents the function found by least squares treatment of the data.)

The values of  $pK_1$  and  $pK_2$  for piperazinium ions, namely 5.333 and 9.73<sub>1</sub> at 25 °C, are to be compared with 8.492 for morpholinium ion at the same temperature. Thus the charged  $NH_2^+$  group in monoprotonated piperazine causes the  $pK_1$  value to be less than the  $pK$  of protonated morpholine. This is to be expected, for one positively charged  $NH_2^+$  group should facilitate the dissociation of the other  $NH_2^+$  group. It may be observed, however, that an oxygen atom in the heterocyclic ring is more powerful in its effect on the dissociation of the  $NH_2^+$  group than is an NH group in the ring,  $pK$  for morpholinium ion (8.492) being smaller than  $pK_2$  for piperazinium ion (9.73<sub>1</sub>).

(H. B. Hetzer)

## B. Dissociation Constants of Substituted Anilines and Phenols

The dissociation constants of substituted anilines and phenols, and particularly of the nitro-substituted compounds, are of interest to the Section, partly in its search for new indicators and partly in the study of the effect of structure on the dissociation equilibria. Data for 4-chloro-2-methylaniline, 2,4-dibromoaniline, 2,6-dibromoaniline, 2-methyl-5-nitroaniline, 4-methyl-2-nitroaniline, and 4-methyl-3-nitroaniline and the corresponding disubstituted phenols have been obtained [39].

The results are shown in figure 12, along with some data for the six dichloroanilines and the six dichlorophenols and a number of monosubstituted anilines and phenols. It is evident that, with some exceptions, there is a linear relation between the  $pK_A$  value of a substituted aniline ( $pK_A$ ) and that of the corresponding phenol ( $pK_P$ ). This linearity might be useful in providing at least an approximation to the unknown value of a substituted aniline if that of the corresponding phenol were known, and vice versa.

It is, however, the exceptional cases in the figure which are of particular interest. Linearity fails for p-methoxy, o-methyl, and o-nitro monosubstitution. Among the disubstituted compounds, it fails for the 4-chloro-2-methyl, the 2-methyl-5-nitro, and the 4-methyl-2-nitro compounds. In two of these there is an o-methyl group and in the third an o-nitro substituent. Thus any anomalies in the monosubstituted compounds carry over, more or less unchanged, to the disubstituted compounds.

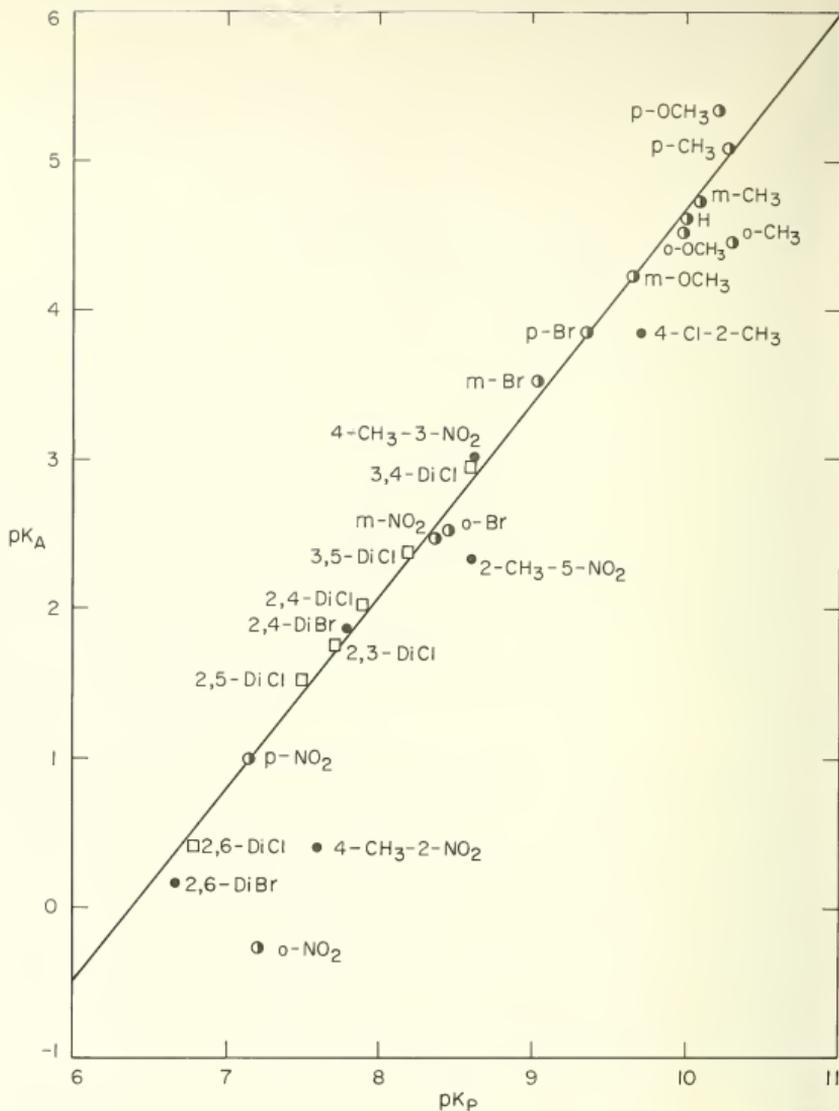


Figure 12. Relationship between the  $pK$  of substituted protonated anilines ( $pK_A$ ) and that of the corresponding substituted phenols ( $pK_P$ ).

As part of a study of the medium effect, the pK values of a number of phenols have been determined in 50 wt percent methanol [40,41]. The pK value is higher in every case in 50 percent methanol than it is in water, as the following results for  $\Delta pK$ , that is  $pK(\text{MeOH-H}_2\text{O}) - pK(\text{H}_2\text{O})$ , show:

<u>o</u> -Nitrophenol	$\Delta pK = 0.687$
<u>m</u> -Nitrophenol	0.615
<u>p</u> -Nitrophenol	0.536
4-Methyl-2-nitrophenol	0.687
2,6-Dichlorophenol	0.889
Pentachlorophenol	0.458

The pK value is, on the average, 0.645 unit higher in 50 percent methanol than in water, but the difference is specific to each substituted phenol.

(R. A. Robinson)

### C. Isopiestic Vapor Pressure Measurements

As part of a program carried out in collaboration with the Office of Saline Water, thermodynamic properties of the following aqueous systems have been determined and the results published:

sodium chloride - barium chloride  
potassium chloride - barium chloride  
sodium chloride - calcium chloride  
magnesium chloride - calcium chloride

Data for the system: potassium chloride - calcium chloride are now being calculated. The support of the Office of Saline Water was terminated November 15, 1966.

(R. A. Robinson)

#### D. Spectrophotometric Studies in N-Methylpropionamide

Acid-base equilibria have been studied spectrophotometrically in N-methylpropionamide at 25 °C for a number of indicator substances of different charge types. Accurate measurements have been made on p-bromoaniline, N,N-dimethyl-p-bromoaniline, m-nitroaniline, 4-chloro-2,6-dinitrophenol, dimethylpicric acid, and metacresol purple. The equilibrium constant at infinite dilution in N-methylpropionamide can be obtained from these measurements. The detailed analysis of results has not yet been completed. Comparison of results with those for aqueous solutions should give useful insights into the nature of solvation in N-methylpropionamide, medium effects, and the effect of dielectric constant.

(Donald Rosenthal)

## 5. CONDUCTANCE AND TRANSPORT BEHAVIOR OF ELECTROLYTES

### A. Objectives and Approach

Transport properties of electrolytes in solution, and electrical conductance in particular, provide information on the behavior of ions that is not obtainable from equilibrium thermodynamics. Practical electrochemical operations, including many analytical methods, must necessarily be carried out under non-equilibrium conditions and may be limited by the rates of the fundamental chemical and physical processes.

Conductance measurements can contribute to an understanding of non-equilibrium properties of electrolyte systems in two ways. First, from a phenomenological approach, such measurements help to define transport, or friction, coefficients. Although the formalism and interpretation of such coefficients is not standardized in practice, it is recognized that they provide a unique, quantitative measure of the pair-wise interactions among the species in a solution as a function of concentration. These coefficients are calculated from an appropriate combination of conductance, transference, and diffusion data. Second, from a mechanistic approach, conductance measurements and current theories concerning them yield estimates of the hydrodynamic properties of ions. An appreciable discrepancy between the Stokes radius of an ion and other estimates of its effective size is usually an indication of specific solvent effects.

Conductance data can also provide thermodynamic data, particularly with respect to ion-pair equilibria. In many nonaqueous solvents these results are not readily obtainable by other means, and in any case the conductance values provide confirmation of thermodynamic data.

A study of conductance cell design has been initiated, using parallel-plate electrodes separated by cylindrical quartz or glass spacers which form the body of the cell. It is anticipated that a wide range of cell constants can be provided by a small selection of interchangeable components. The use of very thin spacers has already proved useful in making cells with low constants and very small volume for monitoring distillations and conductometric titrations. If the constants of such demountable cells prove to be sufficiently reproducible, it may be possible to construct absolute cells in which the conductance of a solution is measured in absolute units on the basis of linear dimensions or capacitance of the empty cell.

(T. B. Hoover)

#### B. Analysis of Errors of the Jones-Dike Conductance Bridge

A commercial Wheatstone bridge based on the design principles of Grinnell Jones [42] is widely used for precise conductance measurements because of its convenience and reliability. Within the operating limits set by the manufacturer [43], namely frequencies below 2 kHz and resistances less than 60,000 ohms, the claimed limit of error of less than 0.02 percent appears reasonable. In order to reduce the effects of electrode polarization, however, it is frequently desirable to extend measurements to higher frequencies. This is especially true when platinization of the electrodes may lead to undesirable adsorption or catalytic reactions.

The Jones-Dike bridge has also been used in this Section for audio-frequency dielectric constant measurements when the cell capacitance is of the order of 1000 pF.

In this application also it is desirable to carry the measurements to higher frequencies in order to eliminate electrode polarization effects. In earlier conductance studies anomalous effects were observed at frequencies greater than 8 kHz with our present bridge. Accordingly, a systematic study was undertaken to identify the sources of error and determine to what extent they could be reduced. The experimental approach was based on an unpublished theoretical analysis due to C. G. Malmberg and outlined below.

In this treatment of the simple Wheatstone bridge, the ratio arms are represented by subscripts 1 and 2, and the unknown and measurement arms by 3 and 4, respectively. Junctions 1-4 and 2-3 correspond to the high potential corners of the bridge. Each arm is represented by a resistance and capacitance in parallel, so that the admittance of arm  $j$  is given by  $Y_j = 1/R_j + i\omega C_j$ . The balance condition  $Y_1 Y_3 = Y_2 Y_4$  is solved with the following approximations:

$$(\omega R_1 C_1)^2 \ll 1$$

$$R_1 = R_2 \text{ (nearly)}$$

$$R_1 C_2 \ll R_4 C_3$$

The difference between distributed capacitances of the ratio arms is given to a very close approximation by

$$C_2 - C_1 = \frac{R_3 - R_4}{\omega^2 R_1 R_4^2 C_3} \quad (33)$$

By placing sufficiently large resistors and capacitors in arm 3 the difference between  $R_3$  and  $R_4$  can be made significant and a very small difference between the ratio arms will be revealed.

Measurements were made at 5 to 50 kHz, with  $R_4 = 50,000$  and 100,000 ohms and  $C_3$  from 600 to 1400 pF. Allowance was made for the losses of the capacitors in calculating the effective parallel resistance in arms 3 and 4. The results showed  $(R_3 - R_4)$  nearly proportional to  $C_3^2$  (rather than to  $C_3$ ), and the external capacitors had much greater apparent loss in arm 4 than in arm 3. The internal circuit of the bridge was examined and found to have been changed from the design specified in reference [43]. The slide wire and end coil ( $R_2$  and  $R_4$  of figure 3 in reference [43]) were shunted by an additional 15-ohm coil. The values of  $R_2$  and  $R_4$  were adjusted so that the effective range of the  $R_2$  dial was -0.05 to 0.15 ohm, but with  $R_2$  set at zero the additional resistance in the measurement arm was nearly 13 ohms. This amount was exactly compensated by an additional coil ( $R_b$ ) in the adjacent (unknown) arm in series with  $X_1-X_2$ . When the ratio arms are closely matched this modification has no effect on the accuracy of ordinary conductance measurements. At high frequencies, however, and with a large capacitance in the unknown arm, the 13-ohm series resistance acts as a frequency-dependent shunt.

Leads from the ends of the new coil,  $R_b$ , were brought to binding posts on the bridge panel so that the coil could be shorted out when desired. Repetition of the tests described above indicated  $(C_2 - C_1)$  was about -2 pF. The introduction of 5-, 5-, and 10-pF silvered mica capacitors in series with each other and in parallel with the ratio coil of arm 2 reduced the indicated unbalance to less than 0.5 pF. With 1000 pF and 100,000 ohms in arm 3 the difference between  $R_3$  and  $R_4$  was 0.05 percent at 20 kHz.

In conductance studies it is frequently desirable to work outside the normal resistance range of the bridge by connecting a resistor of high quality either in series or in parallel with the cell. The external switch panel shown in figure 13 was designed to facilitate the operation and avoid changing lead connections. A reversing switch was included to permit interchanging the cell connections as a check on asymmetry of stray capacitance or inductance. The switches were of an anti-capacity telephone type. A further provision for using either the 2-terminal or 4-terminal mode of cell connection is relatively unimportant with the Jones-Dike bridge because of the slide-wire shunt device used for fine balance. The fixed resistance of this circuit exceeds the usual cell lead resistance which the 4-terminal operation is intended to eliminate.



Figure 13. Switch panel used with conductance bridge to provide a resistor in series or parallel with the cell and to reverse the cell leads.

(T. B. Hoover)

## 6. PREPARATION AND PROPERTIES OF SOLVENTS

### A. Ethanol (95 Volume Percent)

Because of its excellent solvent properties for many organic compounds, 95 percent ethanol (190 proof) finds widespread use in medical, pharmaceutical, and organic chemical fields. At the same time, its water content is sufficient to permit reproducible pH measurements with the glass electrode. Consequently, it is an appropriate medium for investigating solvent effects on electrolytes, both by potentiometric and conductometric methods, and for evaluating pH\* standards.

Published methods for the purification of ethanol usually apply to the anhydrous solvent. They often start with the water azeotrope in order to avoid benzene which may be present in industrial absolute alcohol. The most frequently recommended steps, which may be used in various combinations, are: removal of most of the water with calcium oxide, prolonged refluxing under nitrogen, treatment with silver sulfate or trinitrobenzoic acid, fractional distillation, and removal of the last traces of water by treatment with aluminum amalgam or with magnesium ethylate, followed by a final distillation. Ethanol with by far the lowest conductance that has been reported was prepared by mixed-bed ion exchange treatment of otherwise carefully purified and dried solvent [44].

With a view to simplifying and standardizing the preparation of good quality ethanol, several of the above steps were examined in some detail. Most of them could be eliminated if the deionization treatment were equally effective for stock 190-proof alcohol. A commercial mixed anion-cation exchange resin was equilibrated, with respect to water content of the azeotrope, by continuous extraction

for seven days. The solvent was distilled from a boiler, percolated through the resin and returned by siphon to the boiler. In this way it was expected that water would continuously accumulate in the boiling flask, together with any free electrolyte or soluble organics that might be extracted from the resin. By circulating a limited amount of solvent, it was hoped that the exchange capacity of the resin would not be reduced appreciably. About 40 g of resin (dry weight) containing 60 g of water was treated with 500 cc of 95 percent ethanol. Because of difficulty in controlling the distribution of liquid between the extractor and the boiler, only 150 cc remained in the boiling flask at the end, and the alcohol in contact with the resin contained 15 percent water. U.S.P. 190-proof alcohol having an initial specific conductance of  $6.67 \times 10^{-7}$  ohm<sup>-1</sup>cm<sup>-1</sup> was passed through a column containing the treated resin. The conductance of the product was  $1.43 \times 10^{-7}$  ohm<sup>-1</sup>cm<sup>-1</sup>. Because the latter value was an order of magnitude greater than desired, attention was turned to the preparation of absolute alcohol.

Molecular Sieve 4A was used for the removal of water from U.S.P. 190-proof alcohol. The capacity was about 20 g of water per 100 g of sieves, so that 3.5 l (1 gal) of alcohol required at least 1100 g of the sieves. After standing five days until no more bubbles were released from the drying agent, 2.5 l of alcohol containing 0.35 percent water was decanted. An additional 350 cc was recovered by room-temperature distillation, but this material apparently underwent some dehydration and polymerization. In order to regenerate the sieves, it was necessary to boil them with repeated changes of distilled water until no more odor of ethanol was evident before drying at 250 °C.

The decanted alcohol, which contained considerable fine particulate matter from the sieves, was held at reflux temperature for 20 hr while argon was bubbled through the liquid continuously. Distillation through an efficient, glass-packed column gave a product (A) having a specific conductance of  $1.0 \times 10^{-7}$  ohm<sup>-1</sup>cm<sup>-1</sup>. Distillation from 0.05 percent trinitrobenzoic acid gave a conductance of  $1.6 \times 10^{-8}$ .

Refluxing product A (above) over magnesium ethylate and distillation under argon atmosphere gave material with a water content less than 0.01 percent and specific conductance of  $3.08 \times 10^{-8}$  ohm<sup>-1</sup>cm<sup>-1</sup>. Amalgamated aluminum foil seemed relatively ineffective as a drying agent because of the difficulty in keeping an active surface during the reflux period.

#### B. N-Methylpropionamide

N-Methylpropionamide (NMP), a solvent with a high dielectric constant, has been used in the Section for conductance, viscosity, and kinetic measurements. During the past year the material has been characterized more fully in terms of its physical properties. Densities and dielectric constants have been measured from the freezing point (-30 °C) to 150 °C. All samples used for the recent measurements were reclaimed by fractional distillation from old stock, but several different distillations showed no difference in properties. The water content by Karl Fischer titration was 0.002 percent. The dielectric constant was remeasured on one sample that had been prepared and measured six years ago. The agreement with both the original value and the recent series was excellent. Except for the range 20 to 40 °C, all measurements were made by C. G. Malmberg.

Densities were determined in two dilatometers and checked between 20 and 40 °C with two different pycnometers. All results are represented within 0.005 percent by the equation

$$\begin{aligned}d_4^t = & 0.95069 - 8.136 \times 10^{-4} t + 2.921 \times 10^{-7} t^2 \\ & - 1.79 \times 10^{-9} t^3\end{aligned}\quad (34)$$

where  $t$  is the temperature in °C.

Dielectric constants were determined in three cells, one absolute and the other two relative. One of the relative cells, shown in figure 14, had parallel plate electrodes; the other had concentric cylindrical electrodes.



Figure 14. Cell used for measurements of relative dielectric constants in NMP and NMP-cyclohexane mixtures.

Both relative cells were calibrated with air, nitrobenzene, and water. Measurements were made both with a Jones-Dike bridge and with a General Radio capacitance bridge. The results are represented within 0.2 percent by

$$\log_{10} D = 2.36486 - 5.043 \times 10^{-3} t + 9.846 \times 10^{-6} t^2 - 1.915 \times 10^{-8} t^3 \quad (35)$$

where D is the dielectric constant at t °C.

The binary system NMP-water is of interest because both components are highly polar hydrogen-bonding liquids of different structures. Water appears to be characterized by ice-like pseudo-crystalline aggregates, while the properties of NMP are best explained as due to long chain-wise associations of the molecules. Densities and dielectric constants were measured over the whole composition range and from 20 to 40 °C. The excess molar volumes shown in figure 15 are typical of mixtures of hydrogen-bonding liquids with water, but the minimum is about 10 percent lower than has been reported for any other aqueous system. The dielectric constants show similar large negative deviations. In figure 16 deviations from a linear mole fraction basis ( $D_{12} - N_1 D_1 - N_2 D_2$ ) are plotted against the mole fraction of water ( $N_2$ ) for the sake of compactness. The polarizations, P, calculated for this system are characteristic of strong associations. The P vs. 1/T curve has a large negative slope, but the slope is not quite as great as has been found for methanol or N-methylacetamide. These results suggest that NMP breaks up the ice-like structure of water in favor of the closer-packed monomer structure. On the other hand, water forms hydrogen-bonded crosslinks between NMP chains, resulting in a closer-packed structure with a smaller resultant moment.

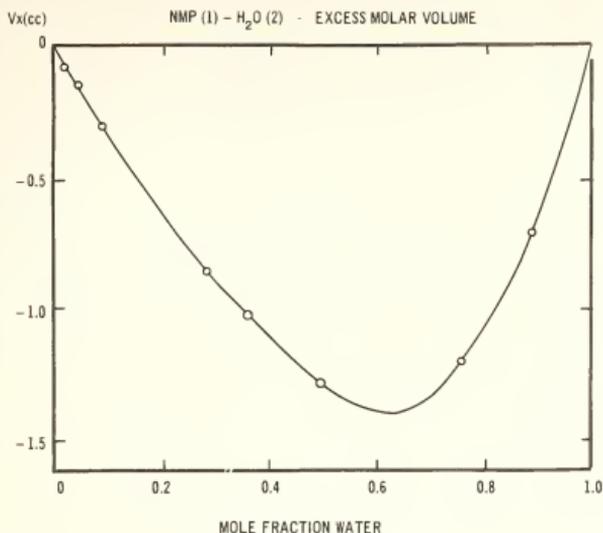


Figure 15. Excess molar volume ( $V_{12} - N_1 V_1 - N_2 V_2$ ) of NMP-water mixtures at 30 °C as a function of the mole fraction of water ( $N_2$ ).

N-Methylpropionamide is miscible with many organic liquids, raising the possibility of a series of binary mixtures isodielectric with water at some one temperature but quite different in other properties. Such a series should help to separate electrostatic from chemical effects in ion-solvent interactions. In order to identify such a series, dielectric constants were measured for mixtures of NMP with cyclohexane, carbon tetrachloride, decalin, and p-xylene. Normal hydrocarbons appear to be incompletely

miscible with NMP. Partial results for one system, NMP-cyclohexane, are given in table 8. Deviations from a linear mole-fraction relationship are slight. Densities are not yet available to show whether the system is more nearly ideal on a volume mixture basis.

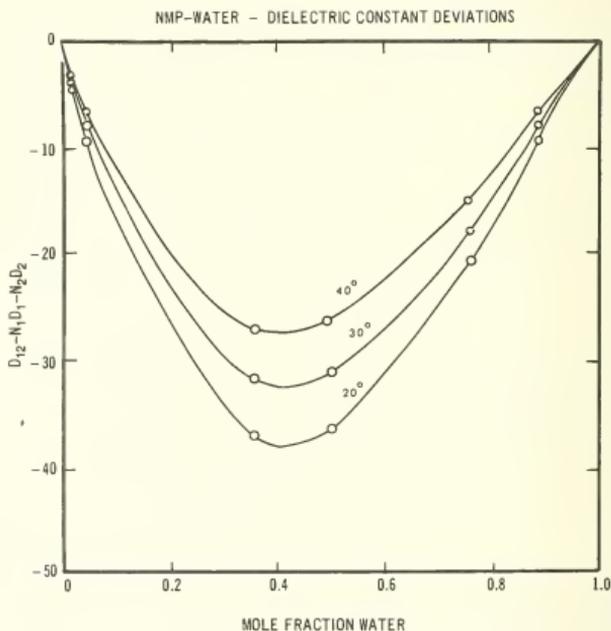


Figure 16. Dielectric constant deviations ( $D_{12} - N_1 D_1 - N_2 D_2$ ) of NMP-water mixtures at 20, 30 and 40 °C as a function of the mole fraction of water ( $N_2$ ).

Table 8. Dielectric constants of N-methylpropionamide-cyclohexane mixtures at 25 °C.

Mole fraction cyclohexane	Dielectric constant	$D_{12} - N_1D_1 - N_2D_2$
0	175.65	0
0.1872	133.77	- 9.38
.3197	109.16	-10.99
.4996	79.34	- 9.56
.7786	33.30	- 7.16
.9522	5.29	- 5.02
1.0000	2.015	0

(T. B. Hoover)

## 7. NONAQUEOUS TITRATIONS:

### DETERMINATION OF HYDROGEN FLUORIDE

An improved procedure for the determination of 5- to 10-mg quantities of fluoride was needed for the assay of calcium fluoride. A pyrohydrolytic procedure was available for decomposing the sample and converting fluoride quantitatively to hydrogen fluoride. The applicable methods in the literature fall into two classes: formation of metal-fluoride complexes, e.g. with aluminum or thorium, and conversion to an alkali salt which can be titrated as a base by various techniques. The direct acidimetric titration of HF in a basic solvent offered the possibility of eliminating several steps.

N,N-Dimethylformamide (DMF) was selected as a promising solvent, and sodium methylate in methanol was chosen as the titrant. Potentiometric, conductometric, and indicator methods for endpoint detection were evaluated. Since water will accompany HF in the distillation from the sample, it is important that moderate amounts of water should not interfere with the accuracy or precision of the method.

Conductometric titrations were made in a circulating cell having a capacity of 20 cc and provided with bright platinum dipping electrodes. The results of four titrations of 5-mg quantities of HF had a standard deviation of 2 percent. The titrant was 0.2 M sodium methylate in methanol. The slope of the conductance curve changed sign at the equivalence point, but the fore-curve was nonlinear and the principal uncertainty lay in defining the intersection of the fore- and post-curves. Up to 10 percent water in the DMF solvent had no effect on the shape of the titration plot, but at the higher water content a fine precipitate formed as the equivalence point was approached. In 50 percent DMF-water no break in the titration plot was discernible.

Potentiometric titrations were made with glass vs. saturated calomel electrodes using an automatic titrator. The same titrant as above was added volumetrically from a calibrated 1-cc buret, and 20 cc of solvent was used in each case. The standard deviation of four titrations of 3-mg quantities of HF was 3 percent.

All of these titrations were made in the presence of two drops of a 0.05 percent solution of phenol red (phenolsulfonephthalein) in DMF. Since the indicator color change seemed to coincide with the instrumental endpoints, further attention was given to optimizing conditions for the indicator titration. Sample and titrant were added by weight from hypodermic syringes and the volume of solvent was reduced to 10 cc. Experience with pyrohydrolysis of fluorspar samples had showed that some tungsten was included in the distillate. To check for possible interference, sodium tungstate was added to some of the samples to give a ratio of tungsten to fluorine of 0.048.

A statistical design was set up with two solvent compositions (1 and 5 percent water) and three different treatments. These were standardization against benzoic acid, titration of HF, and titration of HF plus tungstate. Each combination was run once in a randomized order in five replications of the experiment. Blank titrations were made separately.

The analysis of variance of the results is summarized in tables 9 and 10. The standard deviation for the determination of hydrogen fluoride is consistent with that for the standardizations and corresponds to 1 percent for a single determination. There was no significant effect due to the differences in solvent composition. The highly significant effect caused by tungstate appeared to be

Table 9. Analysis of variance of fluoride titrations.

	Degrees of freedom	Sums of squares of deviations	f
Solvent	1	0.00002738	1.44
Tungsten	1	.0023588	124.2
Blocks	4	.00001095	0.58
Error	13	.00001899	

---

Variate: g NaOMe solution/ g HF solution

Mean: 1.7386

Standard Deviation: 0.0044

Table 10. Analysis of variance for standardization of base.

	Degrees of freedom	Sums of squares of deviations	f
Solvent	1	0.08490	2.44
Error	8	.03487	

---

Variate: g NaOMe solution/ g benzoic acid

Mean: 48.097

Standard Deviation: 0.187

directly equivalent to an alkali correction; that is, the titer of the HF was reduced by the amount of sodium added with the tungstate.

Some preliminary trials were made with solvent containing 10 and 25 percent water. In both cases a precipitate formed during the titration. The blank correction for the 10 percent solvent was remarkably large and variable, and the precision of analysis in the 25 percent solvent was poor.

No trials were made with actual fluorspar samples, but it is anticipated that the HF distillate could be collected directly in a small volume of DMF rather than in aqueous sodium hydroxide as has been the practice. If the tungsten is volatilized as tungstic acid, it may be so insoluble in DMF that it will cause no interference.

(T. B. Hoover)

## 8. FOREIGN-CURRENCY PROGRAMS

The two projects sponsored by the Electrochemical Analysis Section at universities in India and financed through the provisions of the Public Law 480 continued active during the reporting year. A brief description of these programs follows.

A project entitled "Properties of Electrolytes in Nonaqueous Media" is being conducted at Jadavpur University in Calcutta under the supervision of Dr. M. N. Das and Dr. K. K. Kundu. Considerable work is being done on the properties of weak electrolytes in glycol-water solvents over a range of temperatures. During the past year, a manuscript by U. Sen, K. K. Kundu, and M. N. Das entitled "Standard potentials of the silver-silver chloride electrode in ethylene glycol and its aqueous mixtures at different temperatures and related thermodynamic quantities" was accepted for publication in the Journal of Physical Chemistry.

A project entitled "Physicochemical Studies in Non-aqueous Solvents" is being pursued at Panjab University, Chandigarh, under the supervision of Professor Ram Chand Paul. Professor Paul's continuing interests include the behavior of Lewis acids in solvents quite unlike water, ion-pair formation, and the general subject of the solvation of electrolytes. Some studies of weak electrolytes by conductivity methods are also a part of his program.

(R. G. Bates)

## 9. IMPACT OF SECTION'S ACTIVITIES

The impact of the Section's activities can best be judged in terms of the distribution of Section publications, invited talks, and requests for advice and consultation. In this connection, the following statistics, compiled for the calendar year 1966, are pertinent.

Reprints requested . . . . .	1026
Publications distributed without a request . . . . .	1105
Manuscripts reviewed for outside journals . . . . .	55
Project proposals reviewed . . . . .	5
Significant consultations . . . . .	23
universities	8
industries	8
government	4
research institutes	3
Committee memberships . . . . .	16
Publications in 1966 . . . . .	22
Talks given in 1966 . . . . .	18
scientific societies	8
universities	9
government	1

## 10. PERSONNEL

Roger G. Bates, Section Chief  
R. A. Robinson, Assistant Section Chief  
Marguerite Raudenbush, Section Secretary

### Electromotive Force and Acidity Measurements

V. E. Bower (left Dec. 1966)  
J. T. Clark, Jr. (Sept. to Feb.)  
Guest worker, from Clarkson College  
of Technology  
R. Gary (left July 1966)  
Hannah B. Hetzer  
Maya Paabo  
R. A. Robinson  
D. Rosenthal (Sept. to Feb.)  
Visiting Expert, on leave from  
Clarkson College of Technology  
B. R. Staples (reported in May 1967)

### Conductance Measurements

T. B. Hoover  
P. K. Hall (July to Sept.) from the  
University of Wisconsin, Marshfield

### Dielectric Measurements

C. G. Malmberg (left Jan. 1967)

### Isopiestic Vapor Pressure Measurements

V. E. Bower (left Dec. 1966)  
R. A. Robinson

### Kinetic Studies

R. K. Wolford (left July 1966)

## 11. COMMITTEE MEMBERSHIPS

### R. G. Bates

Member, Subcommittee on Hydrogen Ion Determinations,  
ASTM Committee E-1, Sub. 22.

Councilor, American Chemical Society,  
representing the Division of Analytical Chemistry.

Member, NRC Committee on Symbols, Units, and  
Terminology for the Physical Sciences  
(U.S. National Committee for ISO/TC-12).

Member, U.S. National Committee for IUPAC.

Member, Commission on Electrochemistry, IUPAC.

Member, Commission on Symbols, Terminology, and  
Units, IUPAC.

Associate Member, Commission on Electroanalytical  
Chemistry, IUPAC.

Member, Subcommittee on Physicochemical Symbols  
and Terminology, Committee on Physical Chemistry,  
NRC.

Member, Board of U.S. Civil Service Examiners  
(Chemistry Panel).

Member, Advisory Board for Analytical Chemistry.

Member, Board of Editorial Advisers, Analytica  
Chimica Acta.

Member, Washington Editorial Review Board (NBS).

Member, Committee on Units and Usage (NBS).

Member, Museum Committee (NBS).

Member, Advisory Committee on the Senior Lunch Club  
(NBS).

### R. A. Robinson

Secretary, Commission on Electroanalytical Chemistry,  
IUPAC.

12. PUBLICATIONS AND MANUSCRIPTS, JULY 1966 TO JUNE 1967

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2. Stokes, R.H., Robinson, R.A.  
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3. Robinson, R.A., Bower, V.E.  
Properties of Aqueous Mixtures of Pure Salts.  
Thermodynamics of the Ternary System: Water-Calcium  
Chloride-Magnesium Chloride at 25 °C.  
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Properties of Aqueous Mixtures of Pure Salts:  
Thermodynamics of the Ternary System Water-Sodium  
Chloride-Calcium Chloride at 25 °C.  
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Dissociation of 4-Aminopyridinium Ion in 50 per cent  
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 Handbook of Chemistry and Physics. (In Press).

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Medium Effects and pH in Nonaqueous Solvents  
Chapter for Solvation Interactions  
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Nitrophenols in Aqueous Solution at 25 °C.  
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Water-Methanol Solvent Mixtures and Medium Effects in  
the Dissociation of the Protonated Base.  
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13. TALKS, JULY 1966 TO JUNE 1967

1. Bates, R.G., "Solvent Effects on the Dissociation of Protonated Bases", Gordon Research Conference on Analytical Chemistry, New Hampton, N.H. August 25, 1966.
2. Bates, R.G., "Nature of the Solvent Effect of Methanol on the Dissociation of Protonated Tris(hydroxymethyl)-aminomethane" (paper by Schindler, Robinson, and Bates), American Chemical Society meeting, New York, N.Y. September 13, 1966.
3. Robinson, R.A., "The Ionization Constant of Deuterium Oxide from 5 to 50°" (paper by Covington, Bates, and Robinson) American Chemical Society meeting, New York, N.Y. September 14, 1966.
4. Bates, R.G., "The Acheson Medalist, Warren C. Vosburgh, His Life and Career", The Electrochemical Society national meeting, Philadelphia, Pa. October 11, 1966.
5. Bates, R.G., "Acid-Base Behavior in Alcohol-Water Solvents", Chemistry Lecture Series, University of Michigan, Ann Arbor, Michigan. November 10, 1966.
6. Bates, R.G., "Thermodynamic Aspects of Acid-Base Interactions in Nonaqueous Media", Analytical Chemistry Colloquium, University of Illinois, Urbana, Ill. November 15, 1966.
7. Bates, R.G., "Solvent Effects on Acid-Base Processes", Analytical Chemistry Colloquium, Purdue University, West Lafayette, Indiana. November 16, 1966.
8. Bates, R.G., "pH and Other Electrochemical Acidity Functions for Nonaqueous Media", National Capital Section, The Electrochemical Society, Georgetown University, Washington, D.C. December 1, 1966.
9. Bates, R.G., "Acids and Bases in Alcohol-Water Solvents", Passaic Valley Section, American Chemical Society, Montclair State College, Montclair, N.J. January 12, 1967
10. Bates, R.G., "Potentiometric Measurements and pH Standards", Course in Advanced Laboratory Instrumentation, Walter Reed Army Institute of Research, Washington, D.C. March 30, 1967.

11. Bates, R.G., "Medium Effects on Ionic Processes in Nonaqueous Solvents", Symposium on Electrochemistry in Nonaqueous Media, The Electrochemical Society, Dallas, Texas. May 10, 1967.
12. Bates, R.G., "Inner Reference Electrodes and Their Characteristics", Conference on Intracellular Glass Microelectrodes, University of Montreal, Montreal, Canada. May 24, 1967.
13. Bates, R.G., "Ionic Processes and Energies of Transfer from Water to Nonaqueous Media", Chemistry Seminar, McGill University, Montreal, Canada. May 26, 1967.

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